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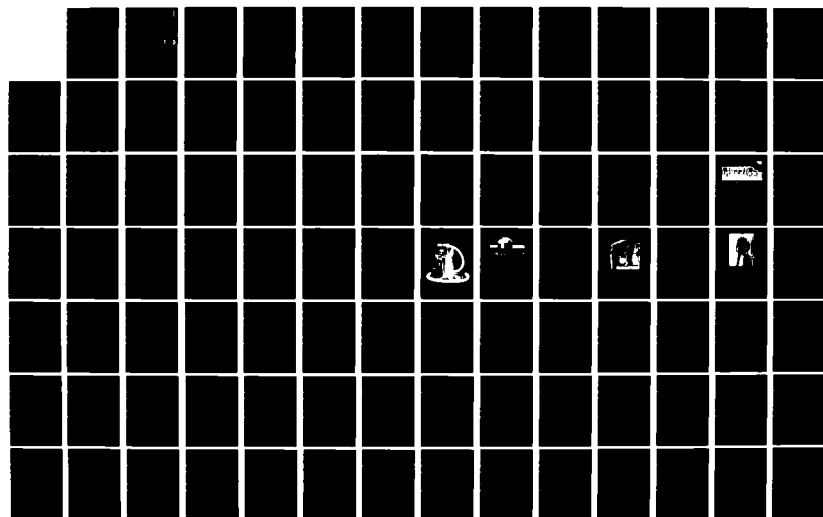
EFFECTS OF WEATHERING ON IMPREGNATED CHARCOAL
PERFORMANCE(U) NAVAL RESEARCH LAB WASHINGTON DC
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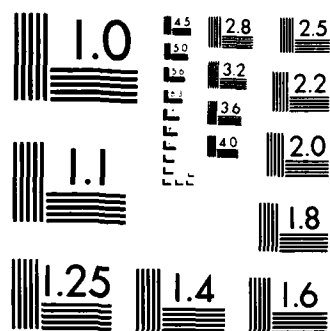
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Effects of Weathering on Impregnated Charcoal Performance

Final Report

Prepared by V. R. Deitz

Naval Research Laboratory

Prepared for
U.S. Nuclear Regulatory
Commission

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Effects of Weathering on Impregnated Charcoal Performance

Final Report

Manuscript Completed: April 1981
Date Published: September 1981

Prepared by
V. R. Deitz

Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, DC 20375

Prepared for
Division of Risk Analysis
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555
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ABSTRACT

The useful life of activated carbon filters in engineered-safety-feature and normal ventilation systems of nuclear power stations is slowly impaired by the contaminants accumulated from the large volume of air in process. In this study eight commercial impregnated carbons were exposed to unmodified outdoor air at NRL for different periods up to one year, each followed by measurements of methyl iodide-131 penetration. The same carbons were also exposed to air flows of known contaminant species and concentrations under controlled laboratory conditions, also followed by measurements of the methyl-iodide-131 penetration. Two of the carbons were exposed to outdoor air at the Atmospheric Physics facilities at the Argonne National Laboratory and at the Simi Valley Monitoring Station of the Air Pollution Control District of Ventura County, California. The test carbons included commercial impregnations of potassium iodide with or without elemental iodine and of tertiary amines, either separately or as co-impregnates. The influence of moisture in laboratory air flows (50, 70 and 90% RH) on the penetration of methyl iodide-131 was studied in detail for the eight carbons. Evidence was found from both the laboratory and outdoor exposure tests that air flows above 70% RH degrade the carbon efficiency significantly. Additional results for the pH and weight changes of the carbons are given. An adverse synergistic influence of moisture and hydrocarbon vapors has been observed. It is believed that local meteorological conditions of high humidity combined with atmospheric pollutants in the test vicinity contribute jointly to the degradation of the trapping efficiencies of impregnated carbons. All test samples were exposed in four one-half inch layers to permit a determination of the profile in properties along the line of flow. The entrance layer was found to be most significantly affected by the exposure insult. The gradient in methyl iodide-131 penetration through the bed changes from a simple exponential profile for new carbons to a non-linear exponential profile for weathered and service-aged carbons. The behavior is attributed to the chromatographic distribution of the contaminants that accumulate in the bed. The thermal stability of KI_x impregnated carbons was studied for the retention of the iodine of impregnation; weathered KI_x carbons were observed to be considerably less stable than new material.

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EXECUTIVE SUMMARY

1. Commercial carbons with TEDA (triethylenediamine) in the impregnation formulation, after exposure to the common contaminants in outdoor air, exhibit less penetration of methyl iodide-131 than do the carbons exposed similarly with only potassium iodine + iodine as impregnant. The behavior was similar at all of the exposure sites employed.
2. The methyl iodide-131 penetration as a measure of carbon-filter performance rises rapidly in air flows greater than 70% relative humidity.
3. The observed influence of water vapor on the degradation of impregnated carbons correlates best with the dew point of the air flow. The trapping efficiency remains good at dew points below about 20°F.
4. The prevailing dew point-temperature-relative humidity at the completion of weathering have a strong influence on the test results. The exposed samples were evaluated for the penetration of methyl iodide-131, weight gain, and the pH of the water extract.
5. Initially, the common air contaminants (ozone, sulfur dioxide, nitrogen oxides, hydrocarbons) adversely influence the inlet layer of carbon in a filter bed. The contaminants then migrate to lower depths with increase of length of service. The use of an additional replaceable carbon, "guard-bed", could extend the useful life of an impregnated carbon filter, if it can be demonstrated to be cost effective.
6. Accidental exposures of a carbon filter to the vapors from solvent spills or to organic vapors from plant operations, contribute to the degradation process more strongly at higher humidities than at lower humidities.

EXECUTIVE SUMMARY (CONT'D)

7. Exposures of KI_x carbons to intermittent flows of outdoor air may yield more penetration of methyl iodide-131 than continuous operations with the same total volume of air. The presence of TEDA in the carbon appears to be stable under continuous and intermittent operations.
8. Weathered samples of carbon cannot be regenerated at ambient temperature by a continued air purge.
9. The laboratory studies indicate that the interaction of ambient concentrations of ozone, sulphur dioxide, or the nitric oxides with impregnated carbons may be of second order importance relative to the insult of water vapor-organic compounds.
10. Exposure times of two to four days to air flows of low relative humidity (<30%) are required to restore the trapping efficiency lost by a previous exposure to air of high relative humidity. Conversely, an exposure time of the same magnitude to high relative humidity is required to degrade the trapping efficiency of a carbon having a low water content.
11. The ASTM test procedures to qualify new impregnated activated carbons for the penetration of iodine-131 or methyl iodide-131 cannot be applied without ambiguity to weathered or service carbons. Additional research is needed to develop such a standard.
12. It is yet to be demonstrated to what degree a carbon bed can be allowed to degrade and still be efficient under postulated accident scenarios. Further studies will be required before a reliable procedure can be developed to establish when carbon filters should be replaced.

I. Introduction

1.1 Objectives

The use of activated and impregnated carbons in the nuclear air cleaning application for periods of two to three years without regeneration is an adsorbent application with new and undefined maintenance problems. During the period in service, the carbon must be ready to serve its role in the retention of radioiodine should an incident occur, as well as for the continuous removal of low concentration levels of radioactive iodine, if present. The carbon may be exposed either continuously or intermittently to atmospheric contaminants and it is not known which of these contaminants is important or how those that are important affect the carbon. The present investigation is, therefore, addressed to several important questions: How can a judgment be made on when the carbon must be replaced? What precursor behavior and information can be used to anticipate the need for a replacement? How can the useful lifetime of the carbon bed be increased? Is the behavior of some carbon impregnant-combinations preferred to others for efficient ¹³¹-iodine retention? The study is, in general, confined to non-accident conditions, i.e., to the normal operating process.

Studies on activated carbons and on impregnated carbons for use in nuclear air cleaning processes have been dominated during the last decade by a need to qualify new materials. Test procedures with this objective (1,2) have been developed. However, the technical evaluation of carbon in-service has proven to be a formidable problem. A carbon is exposed to a variety of environmental contaminants during a long service life without carbon regeneration and these contaminants accumulate and slowly modify the useful life of the carbon. The term "weathering" is used to describe these phenomena. There is no acceptable test whereby an operator of a carbon filter might anticipate a possible drop in the efficiency for trapping radioiodine. The critical penetration may not be observed until the residual iodine retention

efficiency is quite low.

In 1977 the Nuclear Regulatory Commission assigned the task to the Naval Research Laboratory to study the influence of atmospheric degradation of the commercial activated charcoals that are used to trap various species of radioiodine in nuclear power plant ventilation exhausts. In the first reports (3,4,5) from NRL, the many complex factors involved in weathering carbons were discussed. The initial tests were described and the trapping efficiencies for methyl iodide-131 were determined after specific exposure to ozone, sulphur dioxide, carbon monoxide, and water vapor. Tests have since been carried out on a greater variety of carbons with water vapor and/or hydrocarbons utilized as laboratory weathering agents.

In addition to laboratory weathering tests, exposures were conducted using outdoor air at NRL and several other locations. These locations were the Atmospheric Physics facilities of the Argonne National Laboratory, Argonne, IL, the Simi Valley Monitoring Station of the Air Pollution Control District of Ventura County, CA, and in the Auxiliary Building of Unit 2 of the Three Mile Island Nuclear Power Plant, Middletown, PA. Measurements from these sites were included in the study to broaden the data base of important combinations of parameters that contribute to the weathering reactions that degrade the efficiency of the carbon for trapping radioactive methyl iodide. The author is most grateful for the permission granted to use the above facilities.

From a long range safety point of view there is a dual goal in the present investigation. The studies could lead to a longer productive cycle for the carbon filters used in a power installation. At the same time the Nuclear Regulatory Commission would attain an assurance of the required protection against iodine-131.

1.2 Early Application of Activated Carbon in Nuclear Installations

It was recognized quite early in nuclear power activities that air flows contaminated by gaseous fission products

usually cannot be vented directly to the atmosphere. The first application of activated carbon to air cleaning processes appears to be in the trapping of radioactive krypton and xenon. Adams, Browning, and Ackley (6) in work started at the Oak Ridge National Laboratory in 1955 (7) reported on the use of coconut charcoal to retain the krypton and xenon released during the operation of the Oak Ridge Homogeneous Test Reactor. The carbon was not impregnated. This pioneering work has since led to the present cryogenic unit processes with deep beds of activated carbon.

Under the U.S. Atomic Energy Act of 1954, activated carbon played a small role in the effort to decrease iodine risks to an acceptable level. The elimination of elemental iodine was the main objective. For example, in the licensing and regulation of the NRL Research Reactor in 1959, carbon (1-1/8 inch deep) and HEPA particulate filters were specified. The carbon was not impregnated.

Shortly after the krypton and xenon studies, attention was centered on methods for removal of elemental iodine, both gaseous and that contained in particulate material. The removal of elemental iodine vapor in plant systems was shown to be effective using unimpregnated activated carbon. The studies at Oak Ridge of Adams and Browning reported in 1960 and 1962 (8) were concerned with elemental iodine vapor adsorption.

The development of impregnated activated carbons for nuclear air cleaning was also undertaken at the Oak Ridge National Laboratory. In order to trap a penetrating iodine species (locally termed "slick iodine" and later identified as organic iodine compounds), the investigators used a carbon produced by the Mine Safety Appliance Company (MSA) for gas mask canisters. The impregnation contained potassium iodide (9). The carbon was found to be efficient for trapping methyl iodide at high relative humidities (90-95% RH) (10,11). The MSA material was among the first of many adsorbents which are now available and designated as "KI_x impregnated carbons".

The pioneering report of Collins, Taylor and Taylor (12) in 1966 introduced tertiary amines as a viable impregnation

on activated carbons. They also recommended a double impregnation, namely KI and triethylenediamine (TEDA), for application in some reactor containment systems. The activated carbon was a coal-base product, but coconut carbons are now also used. The development of TEDA-impregnated carbons followed from an intensive research program instigated by the United Kingdom Atomic Energy Authority after the Windscale incident of October 7, 1957. Considerable improvements in both the carbon and carbon adsorbers have since been made.

The regulatory guides of the U.S. Nuclear Regulatory Commission now distinguish between atmospheric cleanup systems during normal plant operations (Regulatory Guide 1.140, Revision 1, Oct. 1979) and those systems to be used in a postulated design basis accident (Regulatory Guide 1.52, Revision 2, March 1978). At present the test procedures for the new activated carbon added to both systems are the same, although the performance for representative samples taken from service have a somewhat lower acceptance level. The development of test procedures for carbons in service is being actively pursued by the D-28 Subcommittee of the ASTM and the present report may have a strong bearing on the problem.

1.3 Approach

Impregnated activated carbons representative of those currently used in U.S. nuclear reactors have been used in this study. Hereafter, these will be referred to either generally as test carbons, or specifically by the manufacturer's designation for the carbon.

A two-fold approach has been followed in order to obtain the necessary data base. First, the test carbon samples have been exposed to unmodified outdoor air for various periods of time and at different locations. These were then examined for changes in methyl iodide penetration with $^{131}\text{I-CH}_3$, weight changes, pH of the water extract, and other pertinent chemical properties. This approach is representative of conditions which might exist during the normal service life of a carbon bed, but it does not

allow control over the concentrations or type of atmospheric contaminant. In the second approach, additional samples of the same test carbons were exposed under controlled laboratory conditions to various known pollutant combinations. In this way, pollutant types, concentration, and combinations can be varied under the discretion of the investigator.

The term "weathering" may be placed in better context by distinguishing three mechanisms which result in reduced capability of carbons for removing radioiodine in the nuclear application. First, the term "ageing" of a carbon connotes possible shelflife of the carbon, stored as it must be in closed containers in a given gaseous environment. Thus, ageing would be restricted to a static testing operation. Second, "service-aged" carbon indicates the exposure of a carbon to the actual air flow from a confined system such as a reactor building, fuel-handling building, etc. In fact, the term itself suggests exposure under a pertinent and relevant set of conditions. Third, "weathered" carbon signifies an exposure to ambient contaminants in either a flow of outdoor air at a given location, or under some laboratory set of conditions, where a controlled exposure to a given contaminant can be realized. From the above point of view, a service-aged carbon is a special, and relevant, case of weathered carbon. Under normal operating conditions, the two cases can be identical.

II. Reactants in the Weathering Process

2.1 Contaminants of the Air

The gaseous contaminants used in the controlled laboratory tests were those known to be present in nuclear plant atmospheric environments and for which some adsorption degradation could be expected. The individual species were added in known concentrations to the air flow through a test carbon and the insult concentration adjusted to a small fraction of the adsorption capacity of the carbon. In the alternative approach using large volumes of outdoor air, which are relevant to the application, the same contaminants are present, but the concentrations can vary continuously. A contaminant concentration of 1 ppm becomes a significant insult when integrated over the total flow during the lifetime of a carbon filter.

The environmental contaminants include the volatile hydrocarbons, ozone, sulfur dioxide, nitric oxides, and carbon monoxide, all of which are widely distributed. Local contaminants may also be drawn into the air ducts of a system which lead to the carbon filters as a result of solvent spills, evaporation of lubricating agents, and volatilization of paint components. The prolonged exposure of carbons to these contaminants has a degrading influence on the trapping efficiency for methyl iodide-131, which is the species generally considered as the most difficult radioiodine to remove from nuclear power plant atmosphere. Organic iodides may be generated by a series of chemical reactions between elemental iodine, a fission product, and the organic compounds present in the containment and other structures. The adsorption sites of an activated carbon occupied by atmospheric contaminants are not then available for a reaction with methyl iodide. The specific chemical sites in the interface between the base charcoal and the impregnants, where chemical reactions with methyl iodide molecules take place, can be physically damaged or destroyed. Both types of change occur in "weathering" of charcoals and there has not been hitherto (as of January 1977) an in-depth engineering analysis of the problem.

Table 1. Monthly Average of Pollutant Concentrations (ppm) during 1977, 1978, 1979 - NRL

Month	O ₃			SO ₂			NO ₂			RHC			CO		
	1977	1978	1979	1977	1978	1979	1977	1978	1979	1977	1978	1979	1977	1978	1979
Jan.	0.007	0.013	0.006	0.052	0.028	0.028	0.018	0.011	0.024	0.28	0.04	0.06	1.92	1.45	1.42
Feb.	0.010	-	0.009	0.028	-	0.019	0.055	-	0.028	0.48	-	0.04	1.22	-	1.67
Mar.	0.012	-	0.006	0.023	-	0.026	0.079	-	0.026	0.24	-	1.02	3.77	-	1.80
Apr.	0.013	0.034	0.032	0.023	0.016	0.017	0.051	0.087	0.021	0.40	0.02	0.95	0.63	1.10	1.75
May	0.015	0.037	0.027	0.020	0.013	0.015	0.047	0.031	0.010	0.22	0.10	0.12	0.32	1.24	1.08
June	0.020	0.052	0.032	0.020	0.014	0.013	0.116	0.006	-	1.06	0.05	0.28	0.98	1.06	0.98
July	0.040	0.035	0.034	0.023	0.014	0.013	0.078	0.025	0.035	0.07	0.07	2.53	0.95	1.06	1.59
Aug.	-	0.038	0.034	-	0.015	0.012	-	0.011	0.019	-	0.06	0.32	-	1.25	0.96
Sept.	-	0.030	0.023	-	0.024	0.013	-	-	0.022	-	0.02	0.26	-	1.14	1.26
Oct.	0.018	0.055	0.016	0.015	0.024	0.015	0.073	-	0.023	0.08	0.09	0.32	1.14	1.56	1.63
Nov.	0.013	0.012	0.017	0.015	0.029	0.018	0.028	-	0.033	0.04	0.28	0.44	1.17	2.25	-
Dec.	0.012	0.006	0.013	0.022	0.017	0.022	0.061	0.015	-	0.06	0.89	0.23	1.62	1.52	1.99
Year	0.014	0.031	0.021	0.024	0.019	0.018	0.058	0.027	0.024	0.25	0.16	0.55	1.33	1.36	1.47

NRL Memo Report 3764, "The 1977 NRL Air Quality Data" by A. Stamulis, 27 pp.

NRL Memo Report 4010, "The 1978 NRL Air Quality Data" by A. Stamulis, 19 pp.

NRL Memo Report 4228, "The 1979 NRL Air Quality Data" by A. Stamulis, 35 pp.

Using the NRL Air Quality Data for 1977, 1978, and 1979 (Table 1)(13), the monthly average concentrations of five common pollutants may be seen to have uniform trends. The NO₂ concentrations were fairly uniform over the year; the SO₂ was greater in the first and fourth quarters than in the second and third; the total hydrocarbons including methane were uniform over the year. The oxidants (mainly ozone) were higher in the second and third quarters. These are some of the facts that have to be considered in any attempt to correlate the weathering behavior of charcoals in outdoor air during long periods of exposure.

The reported concentration of contaminants progressively decrease when calculated for longer time-averaging periods. An example at NRL is given in Table 2. When the species is strongly adsorbed (the isotherm has a sharp knee), the adsorption is complete at all but very low concentrations. The total retained by the carbon can then be obtained by integration over the corresponding duration of the air flow. The useful correlation that is sought will relate the contaminant retention and the residual methyl iodide-131 penetration of the carbon.

Table 2. Maximum Pollutant Concentrations (ppm, V/V) for Different Time-Averaging Periods (1977).

	January		February		March		April	
	1 hr.	5 min.	1 hr.	5 min.	1 hr.	5 min.	1 hr.	5 min.
ozone	0.015	0.016	0.031	0.057	0.026	0.03	0.043	0.044
SO ₂	0.31	0.61	0.208	0.414	0.22	0.47	0.20	0.083
NO ₂	0.07	0.10	0.187	0.198	0.18	0.21	0.15	0.16
Total hydrocarbons	5.2	12.0	12.2	28.0	7.7	14.0	5.4	16.0
methane	5.2	16.0	10.4	19.0	6.4	13.0	5.5	12.0
CO	7.1	8.0	7.0	8.2	9.8	27.0	3.4	4.6

Although the individual contaminants may be less than 1 ppm, the volume of filtered air is so huge that upon integration over an operating time a sizable quantity of contaminant may enter a carbon filter. Using a typical reactor system as an example, a flow of 30,000 cfm for 90 days equals 3.9×10^9 cu. ft. directed

through a filter which contains approximately 3750 pounds of nuclear carbon (2-inch depth). The quantities of contaminants introduced to the nuclear carbon of this filter are listed in Table 3.

Table 3. Atmospheric Contaminants Passing into a 30,000 cfm Filter

	Concentration ppmv 3-year av. at NRL	Weight in 90 days (lbs)	Wt. -% of Charcoal
Ozone	0.019	10	0.27
SO ₂	0.023	16	0.43
NO ₂	0.043	21	0.56
CO	1.37	416	11.0
Hydrocar- bons (non- CH ₄)	0.23	214 (hexane)	5.0

It will be shown that CO does not influence the efficiency for trapping methyl iodide-131. Only those hydrocarbons of high molecular weight and some volatility have serious influence. Nevertheless, sizable quantities of contaminants can accumulate in a year's operation when the carbon retains the contaminants. The important question is whether there is a permissible degradation by weathering without jeopardizing the requirement for radioactive iodine removal.

2.2 Moisture Variability of Outdoor Air

An important constituent of the air is the water vapor which in magnitude far exceeds the above-mentioned contaminants. Since the initiation of these investigations (3), the moisture contents of outdoor air encountered at NRL have been recorded for the four seasons of 1977, 1978, 1979 and 1980. The absolute humidity (dew point), Fig. 1, has been maximum in July and August and minimum in January and February (14). The yearly trends are similar and appear to be of a general characteristic of the climatological location of which NRL is a part. The monthly-averaged dew points are below 50°F for about half of the year.

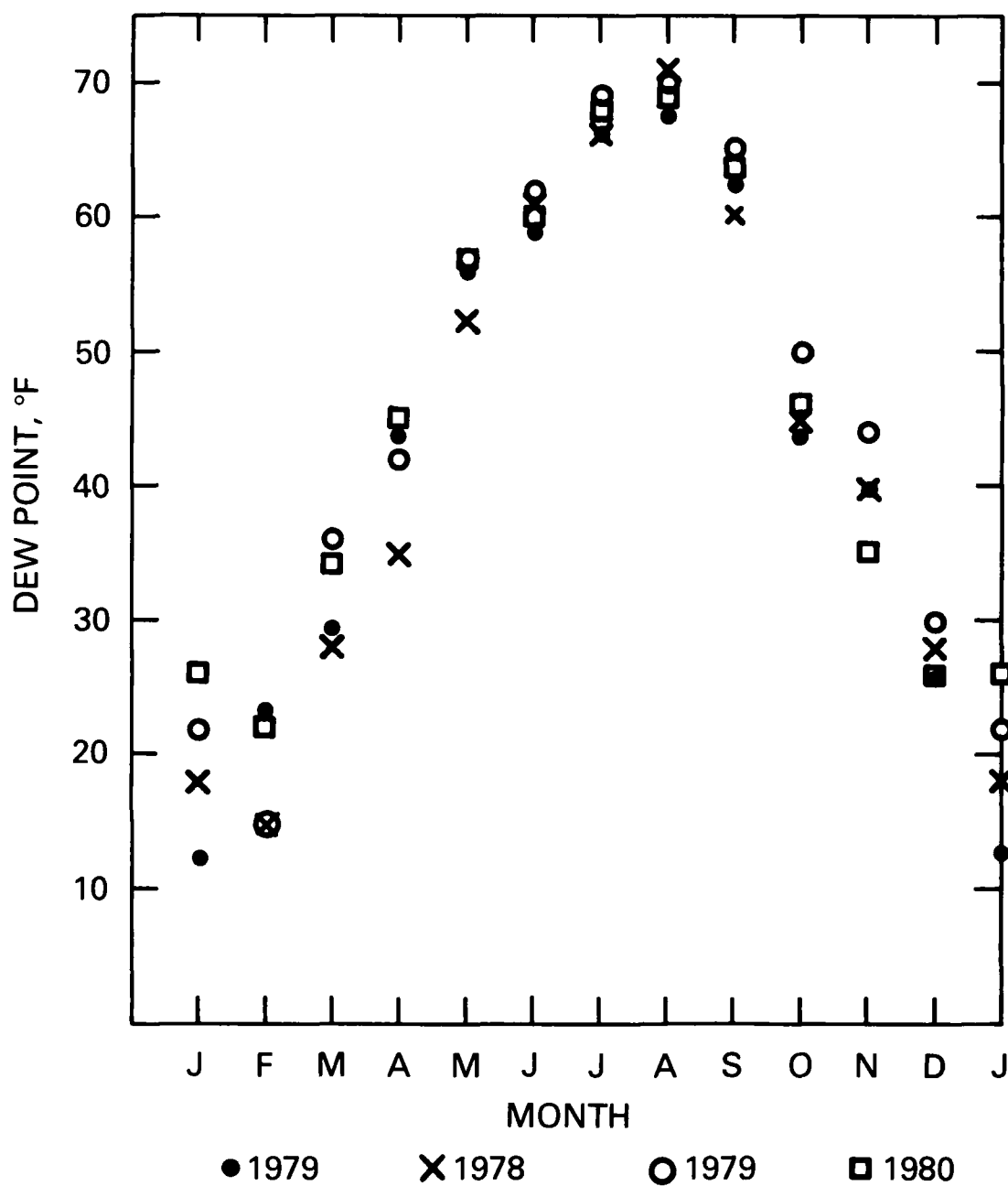


Figure 1. Monthly Average of Dew Points Observed at the National Airport (1977, 1978, 1979, 1980)

The yearly trends of dew point (monthly average) observed at the Chicago O'Hare Airport and at the Argonne National Laboratory are shown in Fig. 2. The maximum also occurred in July and August, but the dropoff is steeper towards lower dew points in the earlier and later months. The carbons were exposed to air flows in the immediate neighborhood of air sampling at the Argonne National Laboratory but there were only small differences compared to the O'Hare Airport station. The averaging over the month hides any local variations.

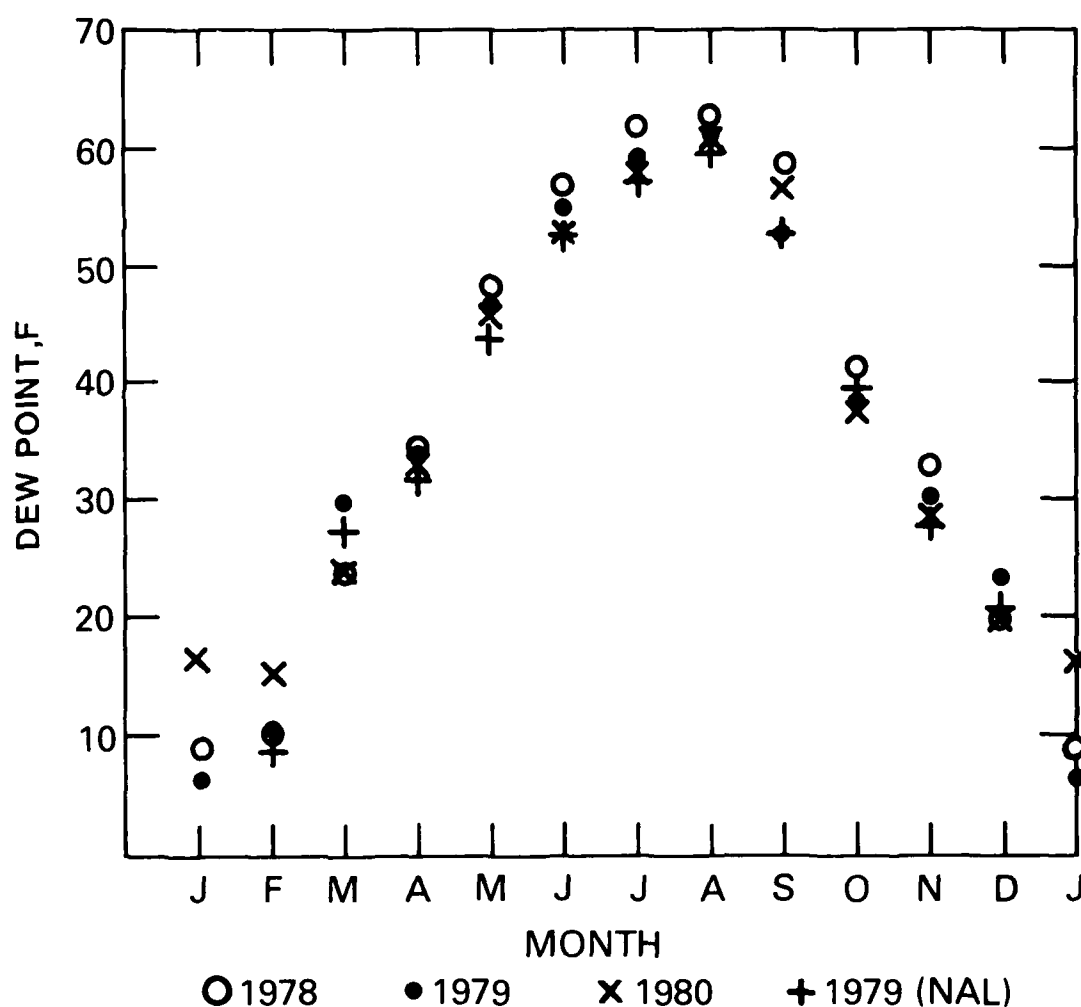


Figure 2. Monthly Averages of Dew Points Observed at Chicago O'Hare Airport and at the Argonne National Laboratory.

A similar situation was observed on comparing the recorded dew points at the Los Angeles International Airport with those calculated for Simi Valley from readings of the local temperatures and relative humidity. The annual trend of dew point (Fig. 3) shows only a shallow maximum in July-August-September, and the total variation over the year was between 60 to 40°F. However, the daily averages may be subject to greater fluctuations, and thus influence the moisture content of the air flow through nuclear carbon.

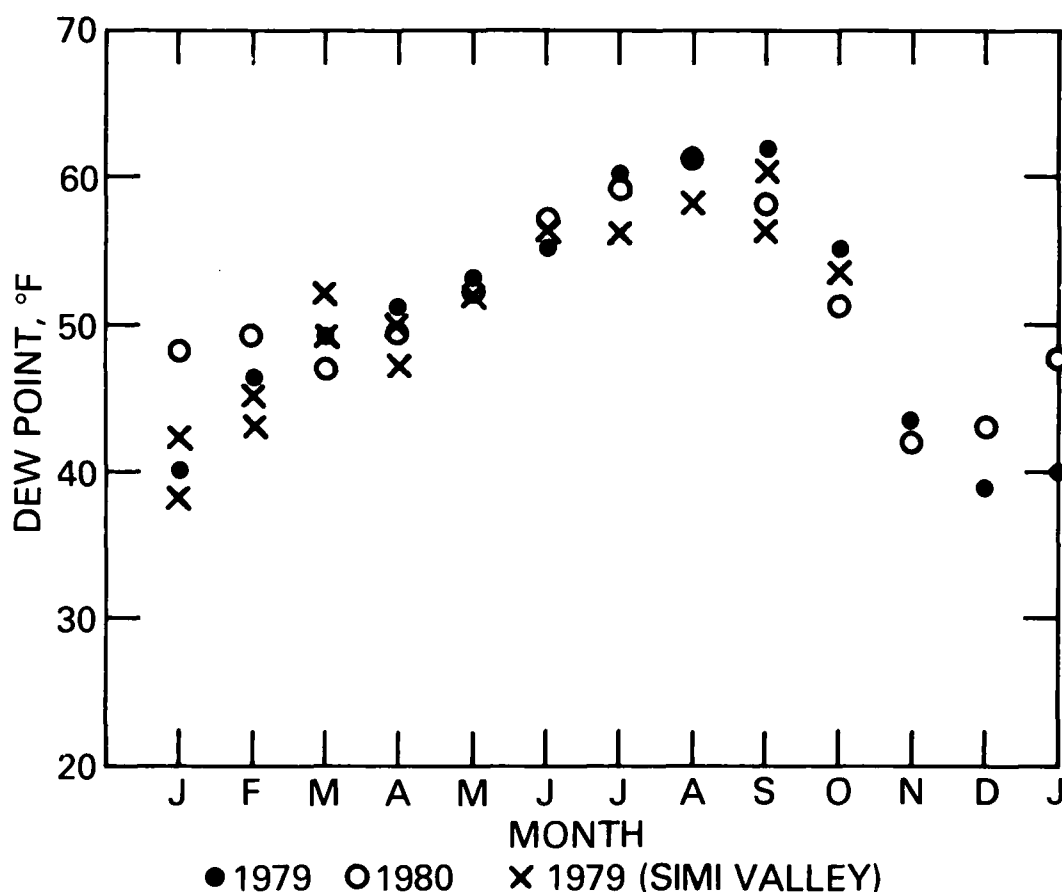


Figure 3. Monthly Average of Dew Points Observed at the Los Angeles International Airport and at Simi Valley, Ventura County, California.

Finally, the dew point trend at the Harrisburg Airport is given in Fig. 4. This location is fairly close to the Three Mile Island Nuclear Power Plant at Middletown, PA. The trend is similar to that observed at the NRL location.

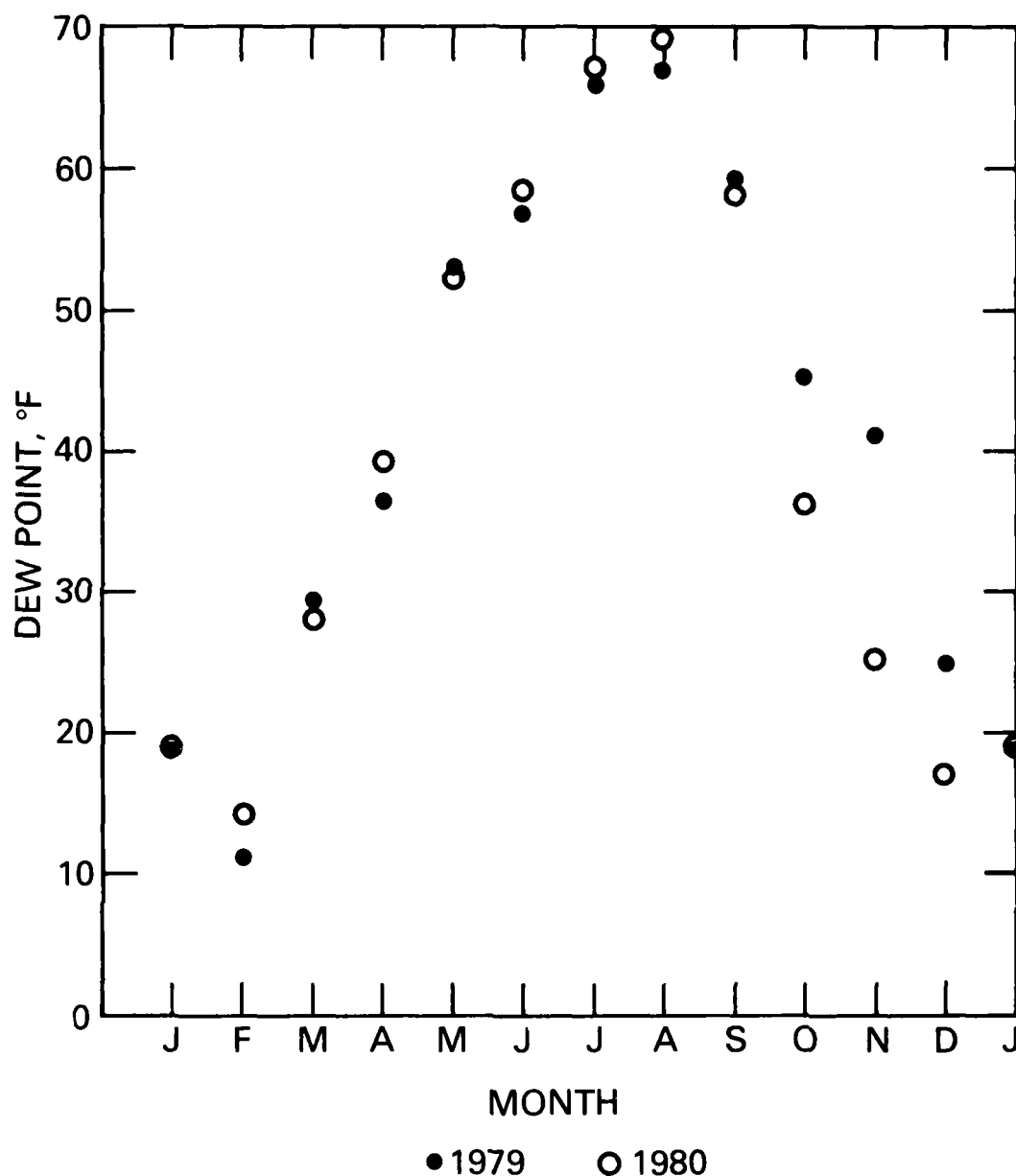


Figure 4. Monthly Average of Dew Points Reported at the Harrisburg Airport near Middletown, PA.

The air-water vapor composition can be characterized by any two of the measurements of temperature, relative humidity, and dew point (see Appendix 1). A plot of water vapor (g/M^3) as a function of dew point ($^{\circ}\text{F}$), given in Fig. 5, shows the strong increase in water vapor concentration with dew point. It suggests that a correlation with dew point may be a helpful parameter in a study of the interaction of water vapor with activated carbon.

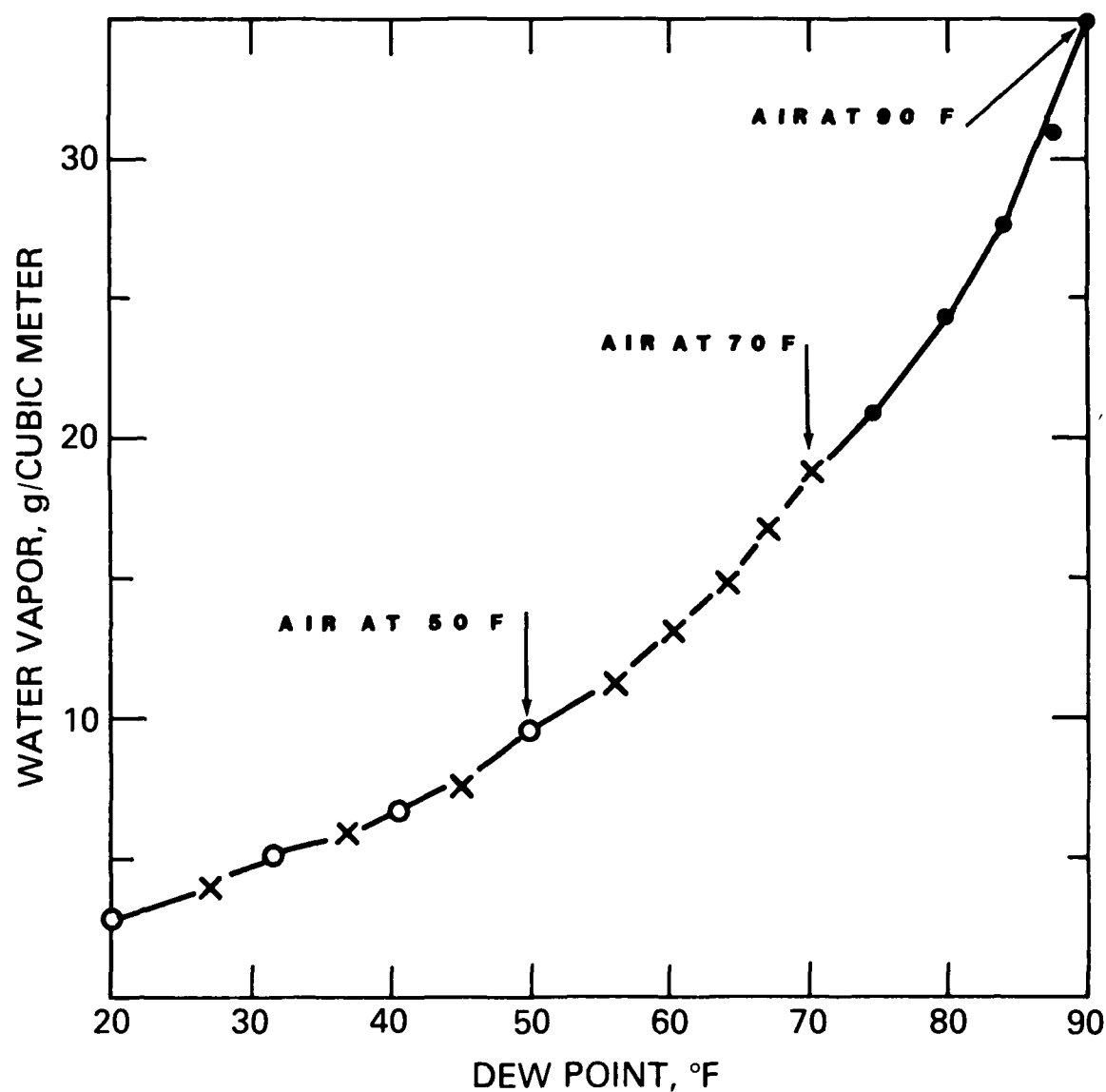


Figure 5. Air-Water Vapor Composition as a Function of Dew Point ($^{\circ}\text{F}$)

The physical adsorption of water vapor at a specified temperature on activated carbon is determined by the relative humidity and controls the mass transfer of the water vapor from a continuous air flow into the adsorbent carbon. On the other hand, the actual partial pressure of water vapor is a measure of the reactant activity in any kinetic rate process and thus determines the rate of chemical reaction of water vapor with the carbon. Hence the dew point, a measure of absolute humidity, is of value in a consideration of the long-range weathering reactions. The $^{131}\text{I}\text{CH}_3$ trapping efficiency of a test carbon after relatively short contact times (24-28 hours) with high humidity air (95% RH) can be recovered by drying the carbon in warm air of lower relative humidity, but prolonged exposures to air flows of high dew point can lead to a degradation that is nonreversible at ambient temperatures (15). The above considerations have suggested that both relative humidity and the dew point be taken into account in the weathering processes of the test carbons.

2.3 Changes in the Base Carbon and in the Composition of the Impregnation

The commercial impregnated activated carbons used by the nuclear industry include both coconut shell and coal as source materials. The impregnations include a mixture of KI and elementary iodine and tertiary amines, either separately or as co-impregnates. The first report (1) dealt mainly with BC 727 and G 615, but the completed study has been extended to include those shown in Table 4. Additional properties of the eight test carbons are given in Appendix 2 and Appendix 3.

The results of this study should be correlated with the properties of test carbons with particular impregnations rather than interpreted as an endorsement or recommendation of any particular manufacturer's product.

Table 4. Impregnated Nuclear Carbons under Investigation

Nuclear Carbon	Nominal Size	CCl ₄ Activity*	Source	Impregnation
BC 727	8x16	90	Coconut	KI + I ₂
BC 717	8x16	60	Coconut	KI + I ₂
G 615	8x16	60	Coconut	KI + TEDA
G 617	8x16	95	Coconut	KI + I ₂
MSA (463563)	8x16	60	Coconut	KI + I ₂
AAF 2701	8x16	60	Coconut	KI + I ₂
KITEG	8x16	60	Coal	Iodine Salts and Tertiary Amines
Sutcliffe, Speakman & Co.	8x16	60	Coal	5% TEDA

*ASTM D3467; TEDA = triethylenediamine

The weathering of activated carbon involves slow chemical changes in both the carbon networks of the activated carbon and in the chemistry of the impregnation. A good working model of the carbon is that of a continuous carbon network of distorted, intertwined ribbons of graphite-like layers which are 3-10 Å thick. This structure is based on a simultaneous analysis of the low and high angle x-ray diffraction studies by Konnert and D'Antonio (NRL) (16). The carbon network also contains smaller quantities of hydrogen, oxygen, nitrogen, and sulfur and these vary with the source material and the method of manufacture.

The impregnation chemicals are subject to a twofold degradation: 1) at the interface between the carbon networks and the impregnates and 2) on the surface of the exposed impregnants. Due to the large surface area of the carbon and the known quantity of impregnation (1 to 5 wt%) the surface coverage by the latter is fractional. Therefore, both the carbon network and the impregnant are subject to the weathering reactions.

III. Weathering of Nuclear Carbons in Outdoor Air

3.1 Naval Research Laboratory, Washington, D.C.

In determinations of the methyl iodide-131 trapping efficiency of new charcoals, a gradient is established along the line of flow and the profile is known to be logarithmic with depth (Figure 6). During the weathering of a charcoal, independent gradients of the retained contaminants are slowly established along the line of flow and these gradients greatly complicate the interpretation of the subsequently measured trapping efficiency for methyl iodide-131. In the present studies this factor has been recognized by dividing the 2-inch depth of charcoal into four equal parts and by making subsequent measurements on each section. While new carbon presents a uniform adsorbent packing to the test gas, namely CH_3I -131, a weathered bed contains a non-uniform or modified adsorbent. A study of the effect of a single contaminant in the four layers may lead to a characteristic and recognizable behavior, but the complexity can be as great for one contaminant as for the entire gamut of atmospheric contaminants. However, a knowledge of the gradient that exists in the four layers is prerequisite to an understanding of multiple contaminant effects.

The stainless steel test container for charcoal weathering, shown in Fig. 7, has an inside diameter of 4 inches and a depth of 2 inches. The bed is separated by perforated stainless steel discs (A) into four equal layers, each of which contains sufficient charcoal for an ASTM test (conducted in a bed 2" diameter and 2" deep). This configuration makes it possible to study the vertical profile of properties through the test sample of charcoal. Two additional perforated discs (B) were installed at each end (B), separated by a spacer 0.5 inches high, in order to equalize the cross-sectional air flow.

The flow rates among different packings of different carbons appear to be related to the fluctuations in packing the 4-inch diameter containers as well as the sieve analyses. Using a ROTON blower (SE2A-14) and the configuration described above,

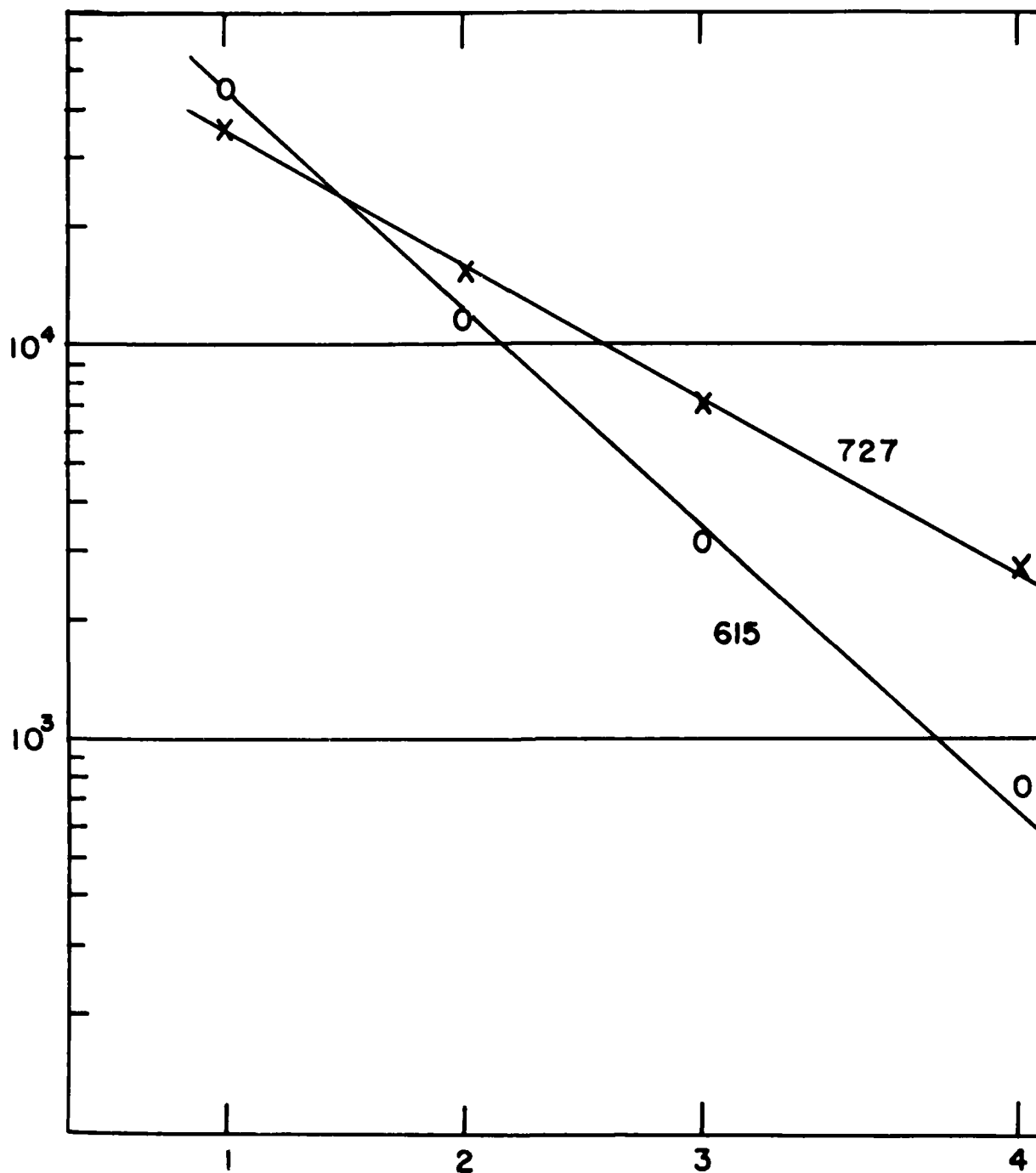


Figure 6. Experimental Depth Profile of $\text{CH}_3\text{I}-131$ with New Carbon in Four One-Inch Layers (Y-axis - counts per second, X-axis - inlet to exit).

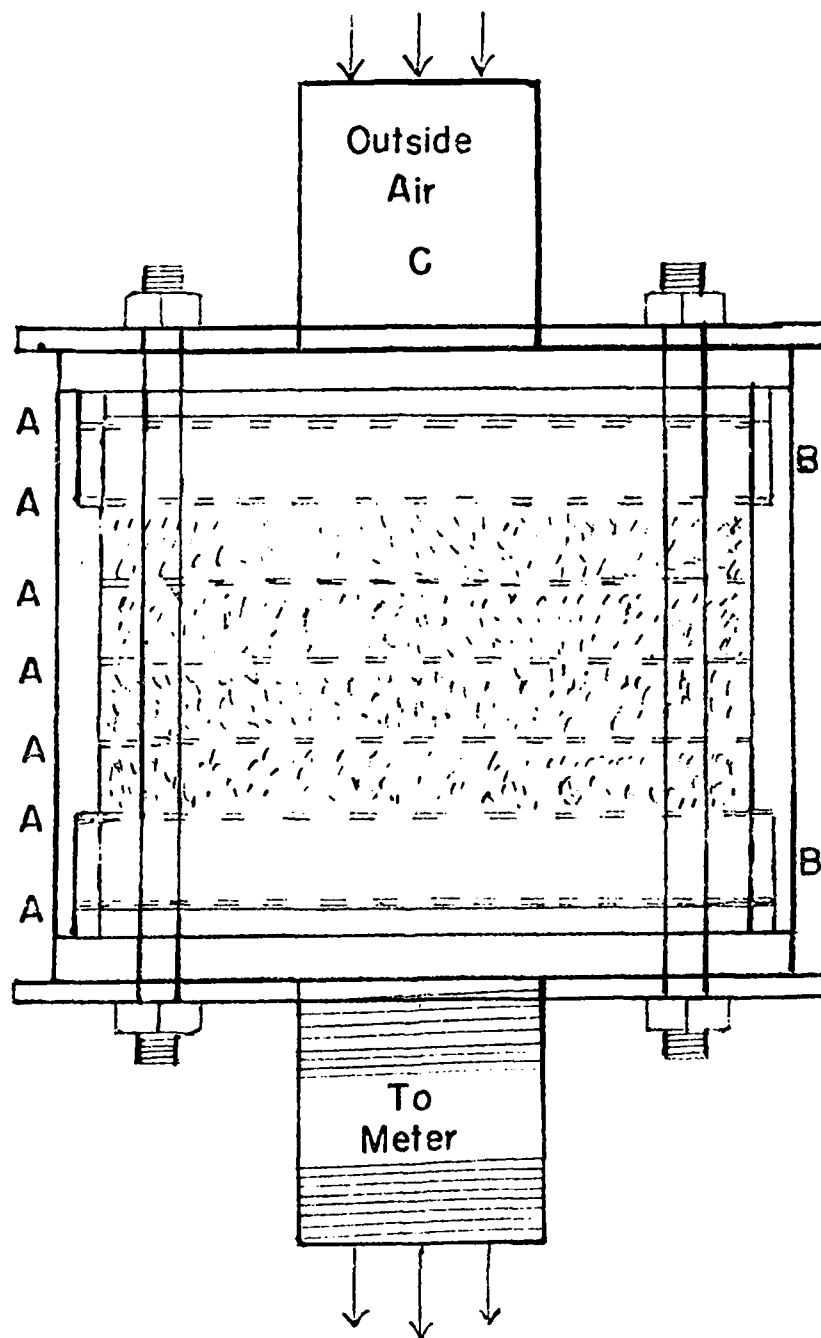


Figure 7. Containers (Stainless) for Test Carbon with Perforated Stainless Steel Separators (A) with Spacer Rings (B) at Entrance and Exit and Inlet and Outlet Tubes (C) 1 3/8 in. I.D.

the mean residence time was 0.344 seconds with a standard deviation of 0.017. This corresponds to a linear velocity of 9 m/min which may be compared to the velocity of 12.2 m/min used in radioiodine test procedures.

A photograph of the assembly at NRL and the geographical location of the exposures are shown in Fig. 8. The pollutants observed at NRL originate in the surrounding areas shown on the map. The air flow was directed in sequence as follows: 1) the air intake above roof (in close proximity to the NRL air analysis intake) to the 12-port manifold located on the top floor of the Chemistry Building, 2) from each outlet port of the manifold through the samples of charcoal, 3) integrating gas meter, 4) intake of air pump, and 5) to ambient air on the top floor. There is a separate gas meter and a separate pump for each sample of charcoal. The initial dry weight and the final weight of each of the four layers were determined in order to follow the gradient in weight changes.

There are several factors that can influence the penetration $^{131}\text{I}-\text{CH}_3$ in a weathered test sample: the integrated insult in the carbon, the particular impregnation of the carbon, contaminant concentration during the exposure, the meteorological and seasonal conditions, especially that which exist at the completion of weathering, and the testing procedure used to determine penetration. Some of these factors have greater influence than others. For example, the results of methyl iodide penetration tests are summarized in Table 5 for a series of 1-month exposures of BC 727 over the indicated dates. Two of 14 values were excessively high and the mean of the remaining 12 values was 0.94% penetration; the standard deviation was 0.82.

Three of the exposures listed in Table 5 (5081, 5082, and 5083) were made simultaneously in the same period 2 May to 2 June, 1978. The mean is 0.813, the standard deviation 0.11, and the variance is 0.009. To the degree that these results indicate good overall reproducibility of the weathering experiment, it is possible to examine the individual exposures in Table 5 for the presence of other interactions which contributed

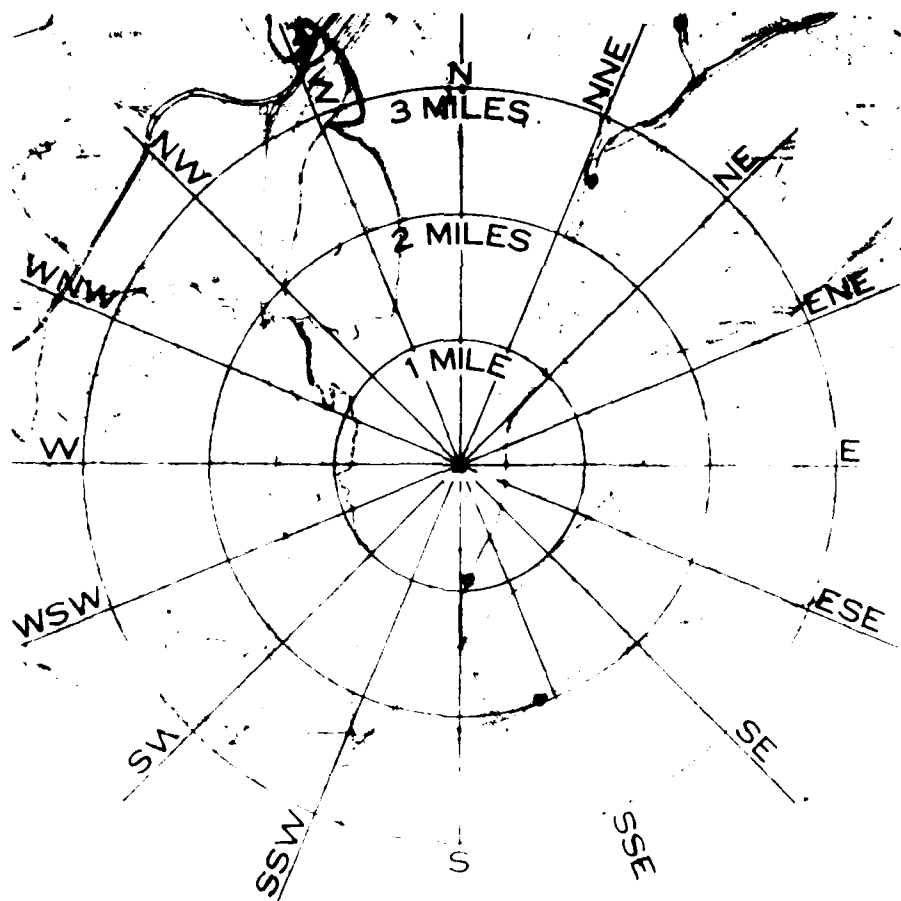
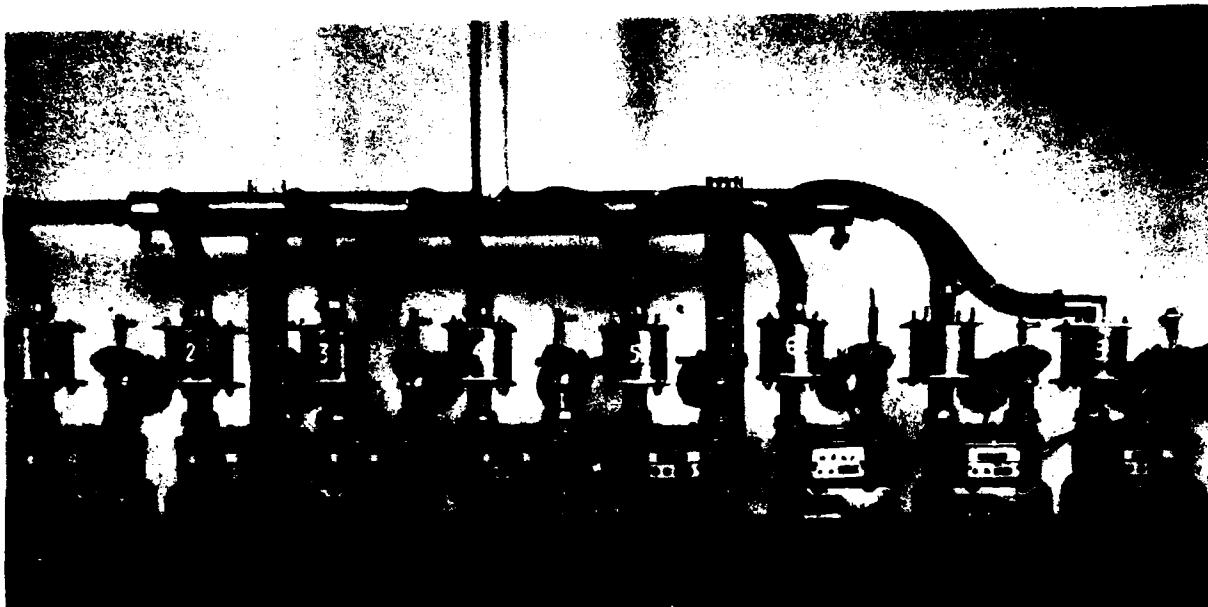


Figure 8. The Assembly used to Weather Test Carbons at NRL and the Geographical Location

to deviations from the overall mean of 0.94. This is done in the following paragraphs.

Table 5. The Penetration of Methyl Iodide-131 after an Exposure for One Month at the Indicated Dates

NRL No.	Penetration %	Exposure
5014	1.30	2 June - 30 June 1977
5070	1.13	7 April - 2 May 1978
5081	0.92	2 May - 2 June 1978
5082	0.69	2 May - 2 June 1978
5083	0.83	2 May - 2 June 1978
5113	13.2	2 Aug - 1 Sept 1978
5121	3.31	1 Sept - 13 Oct 1978
5124	0.81	13 Oct - 14 Nov 1978
5125	0.73	14 Nov - 18 Dec 1978
5126	0.07	18 Dec - 18 Jan 1979
5127	0.81	18 Jan - 21 Feb 1979
5128	0.29	26 Feb - 26 Mar 1979
5130	0.35	27 Apr - 30 May 1979
5150	14.0	30 May - 29 June 1979

High precision is available to count the radioactivity in carbon test beds in the methyl iodide-131 penetration measurements. However, the very low reproducibility in the conditions that exist in weathering charcoals with outdoor air flows makes a comprehensive interpretation of data difficult. High counting precision is, of course, very important in an estimate of the radioactivity that might be present in an iodine release collected by a new charcoal canister.

In a previous section (2.2), it was suggested that a correlation with dew point might be a helpful parameter in studies of the interaction of water vapor with activated carbons. Since the results for the penetration of 131-ICH₃ were obtained for 1-month exposures (Table 5) over the four seasons of the year, a comparison was sought (Fig. 9) for seasonal variations similar to the dew point behavior of Figure 1. Qualitatively, both penetration (Figure 9) and dew point (Figure 1) have a

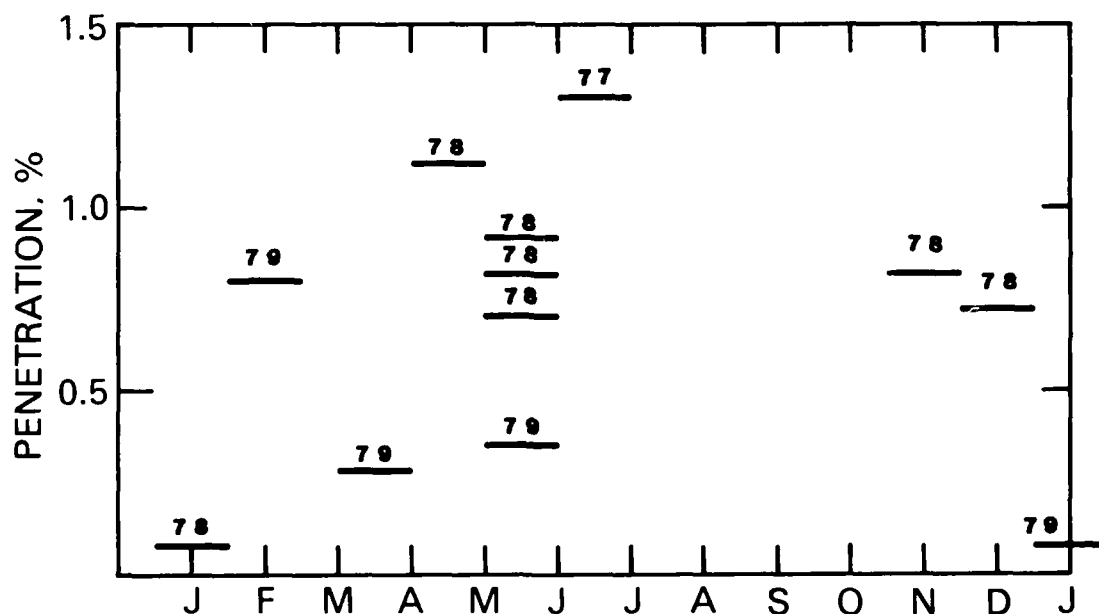
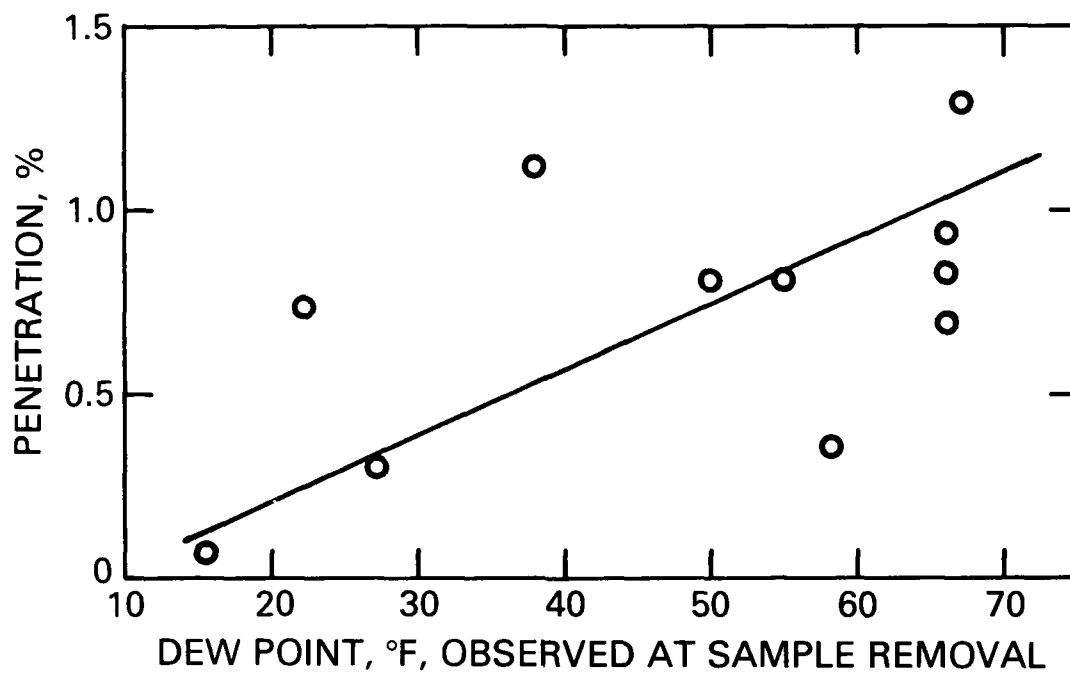


Figure 9. Correlation of Seasonal Dew Point (see Figure 1) with the Penetration of $^{131}\text{I}-\text{ICH}_3$ in Monthly Exposures with the Same Test Carbon (PC 727)

similar dependence. The comparison is not clean-cut because of the fluctuations in dew point during the monthly interval of exposure. The upper graph in Figure 9 presents the penetration as a function of the dew point that existed at the completion time of weathering. There is a trend that indicates a greater penetration at higher dew points. This behavior is compatible with an increase in penetration with an increase in time of prehumidification of a test sample. Also, the weight increases (Table 7) during weathering having a similar seasonal behavior.

The schedule of weathering the various carbons in unmodified outdoor air at NRL is given in Table 6. The exposure dates cover the four seasons in 1977, 1978 and 1979. There is a trend for a somewhat smaller volume of air to pass through a carbon sample in the summer months than in the winter (see plot in Appendix 4). The two carbons, BC 727, typical of KI_x impregnations, and NACAR G 615, typical of a KI_x and TEDA (triethylenediamine) co-impregnations, were followed for 1, 2, 3, 6, 9, and 12 months.

The pH values of the water extracts of charcoals have been determined for all weathered samples, see Table 7. Evans (17) has correlated the progressive decreases in pH obtained for charcoals aged in service with a corresponding decrease in elemental iodine retention of the charcoals. The present work at the Naval Research Laboratory has also established a correlation of pH decrease with increased penetration of methyl iodide-131. It appears, therefore, that the pH of the water extract is a useful measure of relative charcoal degradation and as such is helpful in studies of charcoal weathering. From a fundamental point of view, the surface chemical groups of a charcoal and the adsorbed ionic salts of the impregnation can enter into a series of complex electrolytic reactions with liquid water; when anions are desorbed, hydrogen ions can be formed by hydrolysis and thus lower the pH of the water extract.

The pH data (Table 7) also show the role of the inlet carbon layer as a protective bed to the remaining depth of a carbon. The drop in pH is always greater in this layer than in

Table 6. Weathering Schedule for Test Carbons Exposed to
Unmodified Outdoor Air at NRL

NRL Test No.	Carbon	Exposure Dates	Total Air 10^6 Cu. Ft.	Total Time (months)
5016	NACAR 615	2-30 Jun 77	0.1018	1
5031		29 Jul - 30 Sep 77	.2209	2
5022		1 Jul - 30 Sep 77	.3302	3
5097		3 Jun - 1 Sep 78	.3077	3
5098		3 Jun - 1 Sep 78	.3130	3
5099		3 Jun - 1 Sep 78	.3124	3
5058		16 Nov - 1 May 78	.6288	6
5057		16 Nov - 16 Aug 78	1.0379	9
5133		24 Nov 78 - 5 Sep 79	1.1457	9.5
5123		22 Sep 78 - 25 Sep 79	1.3811	12
5017	NACAR 617	2-30 Jun 77	0.1044	1
5023		1-29 Jul 77	.1017	1
5014	BC 727	2-30 Jun 77	0.1100	1
5070		7 Apr - 2 May 78	.0919	1
5081		2 May - 2 Jul 78	.1143	1
5082		2 May - 2 Jul 78	.1076	1
5083		2 May - 2 Jul 78	.1110	1
5113		2 Aug - 1 Sep 78	.1097	1
5121		1 Sep - 13 Oct 78	.1623	1.5
5124		13 Oct - 14 Nov 78	.1248	1
5032		29 Jul - 30 Sep 77	.2274	2
5065		9 Feb - 7 Apr 78	.2065	2
5096		3 Jun - 1 Aug 78	.2159	2
5020		1 Jul - 30 Sep 78	.3422	3
5056		16 Nov 77 - 1 May 78	.6575	6
5055		16 Nov 77 - 16 Aug 78	1.0105	9
5122		22 Sep 78 - 25 Sep 79	1.3416	12
5113		2 Aug - 1 Sep 78	0.1097	1
5125		14 Nov - 18 Dec 78	.1335	1
5126		18 Dec 78 - 18 Jan 79	.1242	1
5127		18 Jan - 21 Feb 79	.1399	1
5128		26 Feb - 26 Mar 79	.1148	1
5129		26 Mar - 2 Apr 79	.1263	1
5130		27 Apr - 30 May 79	.1098	1
5150		30 May - 29 Jun 79	.1194	1
5156		3 Jul - 5 Sep 79	.2298	2
5084	BC 717	2 May - 2 Jun 78	0.1085	1
5013		2 Jun - 30 Jul 77	.0993	1
5010		1 Apr - 2 May 77	.0826	1
5024		1-29 Jul 77	.1057	1
5019		1-29 Jul 77	.1001	1

(continued)

Table 6 (continued)

NRL Test No.	Carbon	Exposure Dates	Total Air 10 ⁶ Cu.Ft.	Total Time (months)
5039	AAF 2701	1-30 Sep 77	0.1071	1
5040		1-30 Sep 77	.1131	1
5061		16 Nov - 4 Feb 78	.3088	3
5118		17 Aug 78 - 21 Feb 79	.7304	6
5120		18 Aug 78 - 24 May 79	1.1585	9
5042	KITEG	3-30 Sep 77	0.0954	1
5069		9 Feb - 2 May 78	.2952	3
5119		17 Aug 78 - 21 Feb 79	.7738	6
5117		11 Aug 78 - 11 May 79	1.0766	9
5033	Sut. & Speak. (5% TEDA)	29 Jul - 30 Aug 77	0.1204	1
5034		29 Jul - 30 Aug 77	.1259	1
5078		1 May - 1 Jun 78	.1234	1
5079		1 May - 1 Jun 78	.1189	1
5080		2 May - 1 Jun 78	.1138	1
5093		2 Jun - 17 Jul 78	.1746	1.5
5110		18 Jul - 18 Aug 77	.1200	1
5063		9 Feb - 1 May 78	.3160	3
5064		9 Feb - 10 Aug 78	.6736	6
5066		9 Feb - 14 Nov 78	1.0104	9
5015	MSA (463563)	2 Jun - 30 Jun 77	0.1025	1
5021		1 Jul - 29 Jul 77	.0912	1
5060		16 Nov 77 - 4 Feb 78	.3263	3
5059		16 Nov 77 - 1 May 78	.6276	6
5077		1 May 78 - 4 Jan 79	.9699	9

Table 7. Profile Along Line of Flow on Weathering Carbons
at NRL in Unmodified Outdoor Air - pH and Weight
Increase

Test	Months	pH of Layers				% Weight Increase of Layers			
		1	2	3	4	1	2	3	4
NACAR 615									
5016	1	9.3	9.5	9.6	9.7	21.7	19.8	17.0	14.7
5031	2	8.2	9.8	10.0	10.0	21.3	20.7	20.5	17.7
5022	3	7.5	9.8	10.0	10.0	25.9	26.2	26.6	25.7
5097	3	7.9	9.2	9.2	9.3	35.8	35.4	35.4	36.1
5098	3	7.9	9.2	9.2	9.2	36.7	35.3	35.5	35.1
5099	3	7.9	9.2	9.3	9.2	36.0	36.1	36.2	37.1
5058	6	3.8	9.4	9.6	9.6	6.5	4.0	3.2	2.9
5057	9	4.1	8.5	9.2	9.2	36.4	35.0	35.2	35.6
5133	9.5	3.2	8.3	9.5	9.5	35.8	33.3	32.8	32.6
5123	12	2.9	8.7	9.8	9.8	23.6	14.6	13.9	13.6
NACAR 617									
5017	1	8.8	9.4	9.4	9.4	22.2	20.3	18.8	16.9
5023	1	8.4	9.2	9.2	9.2	45.9	46.3	44.9	42.6
BC 727									
5014	1	8.8	9.3	9.3	9.3	25.2	24.0	22.0	20.5
5070	1	8.3	9.2	9.2	9.2	4.9	5.6	5.8	5.8
5081	1	8.4	9.2	9.2	9.2	11.4	19.1	27.8	28.4
5082	1	8.5	9.3	9.3	9.3	12.8	20.0	26.1	26.2
5083	1	8.4	9.2	9.2	9.2	12.9	19.1	19.6	19.9
5113	1	8.6	9.0	9.0	9.0	46.6	47.0	46.8	46.8
5121	1.5	8.0	9.1	9.0	9.0	31.1	36.0	36.6	37.0
5124	1	7.5	8.9	8.8	8.8	33.3	34.7	35.6	35.6
5032	2	7.3	9.3	9.5	9.5	34.8	35.6	34.7	32.2
5065	2	7.3	9.3	9.2	9.4	27.0	24.6	22.2	19.5
5096	2	8.0	9.3	9.4	9.4	46.8	46.6	47.2	48.0
5020	3	7.0	9.4	9.5	9.5	34.5	36.0	35.0	33.0
5056	6	3.1	8.9	9.1	9.0	9.1	3.0	2.6	2.5
5055	9	3.3	8.5	8.8	8.8	47.4	45.1	45.1	44.7
5122	12	2.2	8.2	9.0	8.9	28.9	20.0	19.7	19.6
5113	1	8.6	9.0	9.0	9.0	46.6	47.0	46.8	46.8
5125	1	7.4	8.6	8.7	8.7	3.0	1.7	1.8	1.9
5126	1	7.3	8.4	8.5	8.7	4.7	3.9	3.7	3.7
5127	1	7.2	8.6	8.6	8.7	27.9	23.6	19.9	16.6
5128	1	7.7	8.9	8.9	9.0	5.9	5.0	5.4	5.1
5129	1	8.0	9.0	9.0	9.1	42.1	41.7	41.4	41.5
5130	1	7.9	9.0	9.0	8.9	14.3	29.1	35.1	35.9
5150	1	8.1	9.1	9.1	9.1	30.7	29.8	29.1	27.6
5156	2	7.7	9.1	9.1	9.2	48.5	48.1	48.4	49.0

(continued)

Table 7 (continued)

Test	Months	pH of Layers				% Weight Increase of Layers			
		1	2	3	4	1	2	3	4
BC 717									
5084	1	8.2	9.1	9.1	9.1	16.0	23.7	29.0	30.0
5013	1	8.8	9.2	9.3	9.3	24.1	21.8	20.1	16.8
5010	1	8.5	8.9	9.0	9.2	37.0	36.7	35.5	34.0
5024	1	8.6	8.6	8.9	9.0	35.3	35.5	35.6	35.6
5019	1	8.1	8.6	8.9	8.8	13.2	11.6	11.8	9.9
2701 (American Air Filter)									
5039	1	7.6	8.5	9.1	9.1	27.4	30.2	28.2	25.0
40	1	7.6	8.7	9.1	9.1	26.7	29.4	26.7	22.2
61	3	3.6	8.2	8.5	8.6	5.5	2.0	1.8	1.7
5118	6	2.4	7.0	8.0	8.0	27.0	18.9	16.5	14.8
5120	9	2.5	5.2	7.8	8.0	45.5	41.7	42.7	41.6
KITEG (Nuclear Consulting Services, Inc.)									
5042	1	6.7	9.2	9.6	9.6	16.8	16.2	16.7	17.3
5069	3	2.8	7.2	7.3	7.4	9.2	5.2	5.0	4.7
5119	6	2.4	5.7	6.9	7.0	27.0	20.0	19.1	18.4
5117	9	2.3	5.6	6.6	6.9	29.6	24.1	25.1	25.0
Sutcliffe & Speakman (5% TEDA)									
5033	1	7.1	7.9	7.8	7.9	21.2	15.8	14.7	14.2
5034	1	7.2	8.0	8.1	8.0	14.5	13.7	14.4	14.3
5078	1	8.2	8.6	8.6	8.6	1.0	1.5	6.0	9.4
5079	1	8.1	8.6	8.6	8.6	0.4	1.3	5.8	9.4
5080	1	8.2	8.6	8.6	8.6	0.0	2.3	6.8	9.8
5093	1+	7.7	8.2	8.3	8.3	25.7	26.9	26.3	26.4
5110	1	8.0	8.3	8.3	8.4	19.5	20.8	21.9	21.5
5063	3	4.5	8.7	8.9	8.9	5.9	2.4	2.1	2.0
5064	6	4.0	8.1	8.3	8.4	30.7	28.7	28.5	28.6
5066	9	3.2	7.4	7.9	8.1	26.5	22.2	22.0	22.0
MSA (463563)									
5015	1	7.45	7.65	7.65	7.8	19.8	17.3	14.6	11.8
5021	1	6.7	8.2	8.2	8.2	30.0	30.3	30.1	30.3
5060	3	3.4	7.5	7.7	7.8	5.0	1.9	1.6	1.6
5059	6	2.5	6.9	7.8	8.0	8.0	2.4	1.7	1.6
5077	9	2.7	6.4	6.9	7.3	9.2	1.6	0.92	0.06

three remaining beds. After 12-month exposure, the pH of the top layer of carbon dropped below three, indicating the accumulation of considerable acidic contaminants.

3.2 Exposures at the Argonne National Laboratory, Argonne, IL

In order to expose the carbons to outdoor air at sites other than NRL, portable units to handle two carbon samples were constructed. The unit shown in Fig. 10 was contained in a 20-gallon galvanized can with suitable holes to accommodate the power cable and the air inlet duct. Each sample container was mounted on an integrating flow meter and the intake of the air pump was mounted on the exit of the meter.

Two of these units were placed in an outdoor facility of the Atmospheric Physics Section (Bruce S. Hicks, Section Head), Argonne National Laboratory, Argonne, IL. The author is grateful to Frank Kulhanek of the Atmospheric Physics Section for monitoring the exposures. A photograph of the location at Argonne is shown in Fig. 11.

Table 8. Weathering Schedule for Test Carbons Exposed to Unmodified Outdoor Air at the Argonne Location (Illinois)

NRL Test Sample	Carbon	Exposure Time		Total Air (CF)	Total Time (months)
		On	Off		
5137	BC-727	12 Feb 79	21 Mar 79	142,600	1.3
5139	"	21 Mar 79	22 Oct 79	763,400	7
5164	"	22 Oct 79	27 Feb 80	499,100	4
5138	G-615	12 Feb 79	21 Mar 79	130,600	1.3
5140	"	21 Mar 79	22 Oct 79	716,300	7
5165	"	22 Oct 79	27 Feb 80	473,900	4
5192	S & S 5% TEDA	27 Feb 80	13 May 80	298,800	2.5
5207	"	13 May 80	20 Oct 80	598,900	5.2

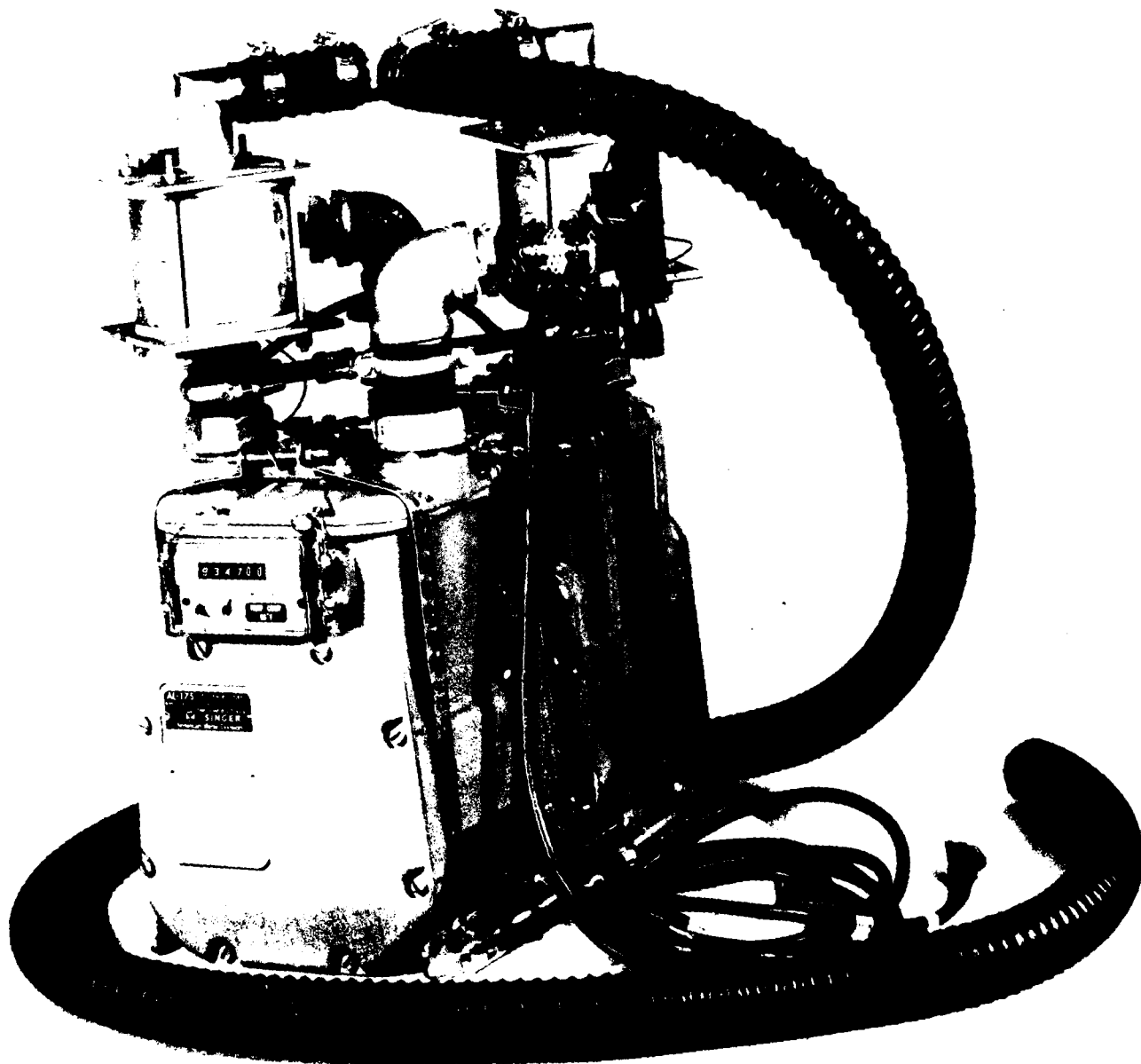


Figure 10. Portable Unit to Weather Two Samples of Nuclear Carbons at Sites Other than NRL

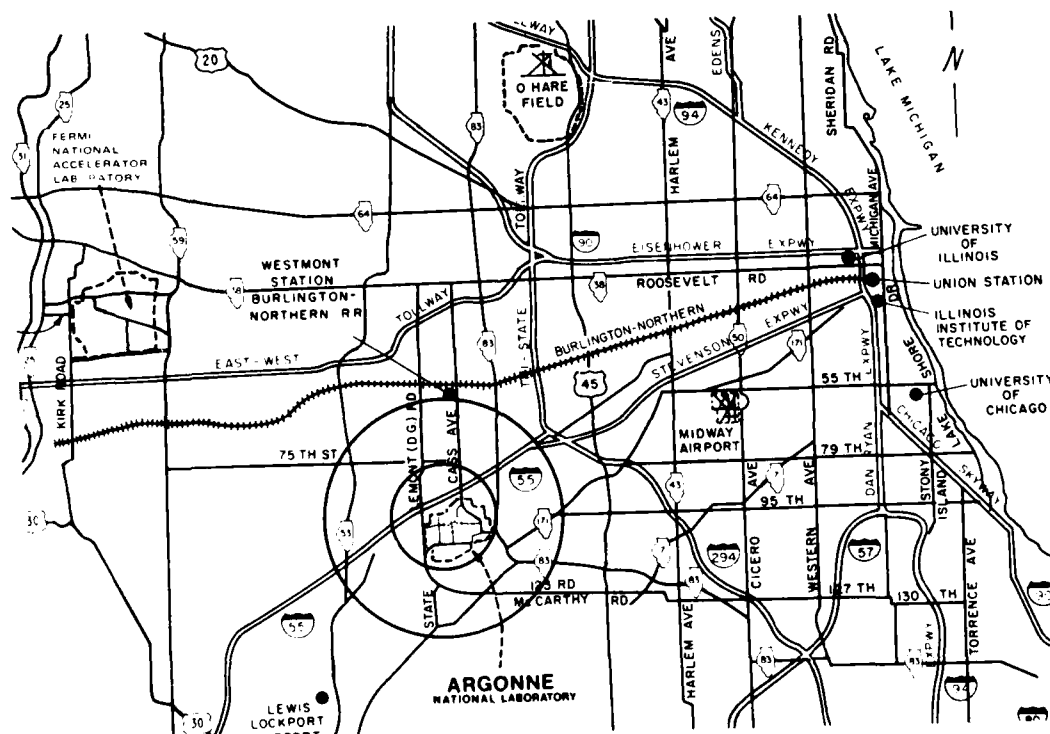


Figure 11. Location of the Carbon Weathering Unit at the Argonne National Laboratory in a Facility of the Atmospheric Physics Section, Argonne, IL

3.3 Exposures in Simi Valley, Ventura County, California

Two of these units were located in the Simi Valley monitoring station of the Air Quality Surveillance, Air Pollution Control District of Ventura County, CA, Douglas L. Tubbs, Manager. The author is grateful to Mr. Irvin Johnson of this staff for monitoring the exposures. A photograph of the location is shown in Fig. 12.

Table 9. Weathering Schedule for the Carbon Exposed to Unmodified Outdoor Air at the Simi Valley Location (California)

NRL Test Sample	Carbon	Exposure Time		Total Air (CF)	Total Time (months)
		On	Off		
5141	BC-727	23 Mar 79	24 Oct 79	824,900	7
5166	"	24 Oct 79	28 Feb 80	514,400	4
5142	G-615	23 Mar 79	24 Oct 79	752,100	7
5167	"	24 Oct 79	28 Feb 80	472,600	4
5195	S & S 5% TEDA	28 Feb 80	14 May 80	312,400	2.5
5208	"	14 May 80	24 Oct 80	646,100	5.3

3.4 Exposures at Three Mile Island, Middletown, PA

An opportunity was provided in late 1979 to install a unit in the auxiliary building of Unit 2, Three Mile Island. This presented a means to weather a charcoal under conditions within an operating building. The weathering unit was placed on the 328 ft. elevation floor where traffic was minimum. The building was under close control and at this point in time the decontamination was nearly complete. Hence, the level of contaminants to the carbon was low and, moreover, the air was warmed to building temperature.

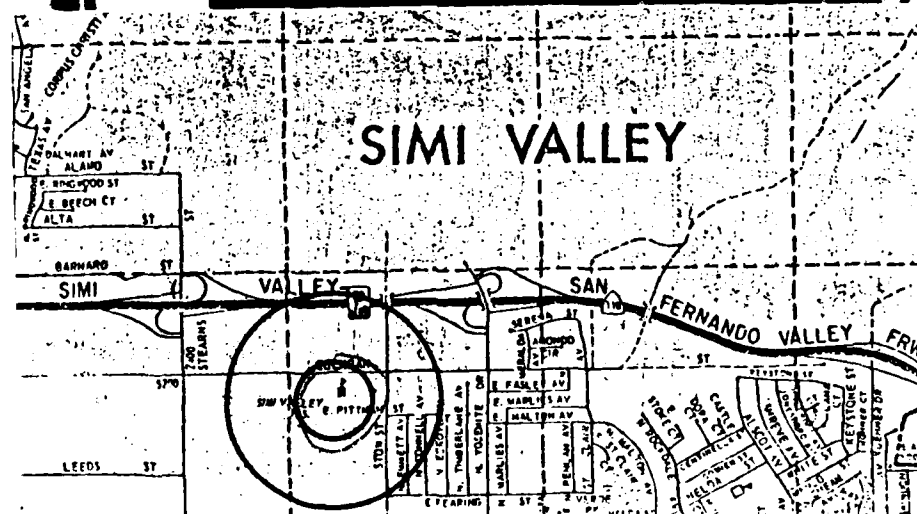


Figure 12. Location of the Carbon Weathering Unit at the Simi Valley Monitoring Station, Air Pollution Control District of Ventura County, CA. Photograph courtesy of Mr. Irvin Johnson.

Table 10. Weathering Schedule for the Carbons Exposed within the Auxiliary Building at TMI

NRL Test Sample	Carbon	Exposure Time		Total Air (CF)	Total Time (months)
		On	Off		
5172	S & S	5 Dec 79	7 Feb 80	335,800	2
5171	G-615	5 Dec 79	7 Feb 80	163,400	2
5190	G-615	13 Mar 80	11 Jul 80	108,500	4
5191	NUSORB-Q	13 Mar 80	11 Jul 80	489,800	4

Figure 13 shows a test carbon weathering unit in place in the Auxiliary Building of Unit 2, Three Mile Island Power Plant of the Metropolitan Edison Company.

3.5 Penetration Results

Three test modes, or configurations, containing the weathered test carbon have been used (3) in the determination of the penetration of $^{131}\text{ICH}_3$. The test bed itself in all cases is 2 inches in diameter and 2 inches in depth. The three modes are:

Mode 1 - Measurements of penetration were made separately with carbon taken from each of the four weathered layers requiring four determinations for each weathered sample.

Mode 2 - Measurements of penetration were made using one-fourth of the carbon from each weathered layer, reconstructed in the test bed in the same sequence of entrance-to-exit.

Mode 3 - Measurements of penetration were made in situ with the carbon weathered in standard test beds. This mode did not require the transfer of the carbon to a test bed.

It is essential to keep in mind that a weathering procedure results in a non-uniform carbon bed. In contrast, the test beds of new carbons are prepared from a uniform sample.

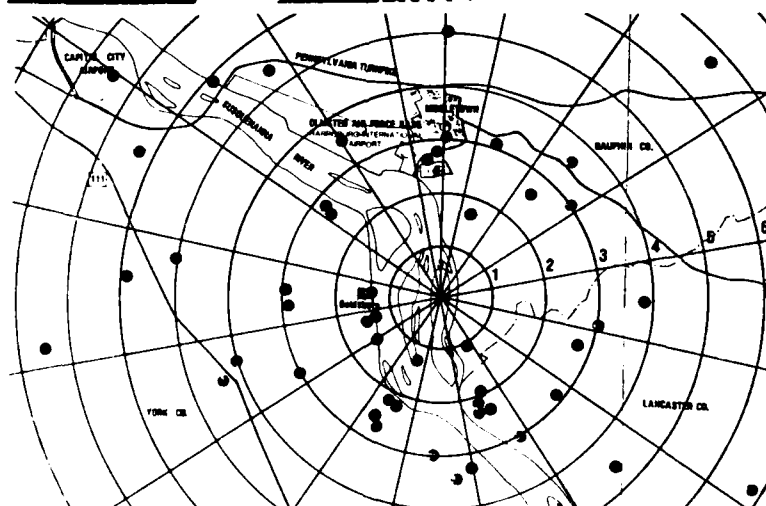


Figure 13. Carbon Weathering Unit in the Auxiliary Building of Unit 2, Three Mile Island Power Plant of Metropolitan Edison Co.

In the present study of weathered samples, the four layers have been handled separately in order to preserve the contaminant gradients and to determine the vertical profile in penetration after the weathering of the test carbon.

Of the three test modes for conducting the penetration test, it is possible to calculate a result for Mode 2 from the four values of penetration obtained by Mode 1. Using the expression for penetration

$$\frac{C_x}{C_o} = \exp (-k_v \tau) \quad (1)$$

$$k_v = -1/\tau \ln \frac{C_x}{C_o}$$

where C_x = penetration concentration, C_o = initial concentration, τ = residence time, and k_v reaction rate constant; the values of k_v are first calculated with the data of Mode 1. In each of these cases, $\tau = 0.25$ sec. Since $\tau = .0625$ in each layer of Mode 2, the penetration is then calculated for each of the four layers using the corresponding value of k_v . Third, the product is calculated for the desired penetration, namely,

$$\text{Product} = \frac{C_1}{C_o} \times \frac{C_2}{C_1} \times \frac{C_3}{C_2} \times \frac{C_4}{C_3} = \frac{C_4}{C_o} \quad (2)$$

Some examples are given in Table 11 using the data for weathered test carbons.

A comparison between calculated and observed penetrations in Mode 2 of the weathered carbon requires that at least two independent samples be weathered under the same conditions. These were prepared using laboratory control in air flows at 100 L/min for 100 hours at 70% RH and at 90% RH. The results, given in detail in Table 12, show excellent agreement between calculated and observed penetrations of $^{131}\text{ICH}_3$ for the carbon (BC 727). The reproducibility of the laboratory weathering procedure is also established by these measurements.

Table 11. Calculation of Penetration in Mode 2 Configuration from the Results in Mode 1 (see Section 3.5)

Test	Weathered Layer	Depth (cm)	Penetration Fraction	τ	k_v	τ	$e^{-k_v \tau}$	Product*
5016	1	5.08	.0177	0.25	16.137	.0625	0.365	0.72%
	2	5.08	.0064	0.25	20.206	.0625	.283	
	3	5.08	.0034	0.25	22.736	.0625	.241	
	4	5.08	.0070	0.25	19.847	.0625	.289	
5031	1	5.08	.0342	0.25	13.502	.0625	0.430	1.41%
	2	5.08	.0132	0.25	17.310	.0625	.339	
	3	5.08	.0086	0.25	19.024	.0625	.305	
	4	5.08	.0102	0.25	18.341	.0625	.318	
5022	1	5.08	.0862	0.25	9.804	.0625	0.542	1.84%
	2	5.08	.0138	0.25	17.132	.0625	.343	
	3	5.08	.0119	0.25	17.725	.0625	.330	
	4	5.08	.0081	0.25	19.264	.0625	.300	
5014	1	5.08	.0267	0.25	14.492	.0625	0.404	1.30%
	2	5.08	.0120	0.25	17.691	.0625	.331	
	3	5.08	.0068	0.25	19.963	.0625	.287	
	4	5.08	.0131	0.25	17.341	.0625	.338	
5032	1	5.08	0.0581	0.25	11.382	.0625	0.491	3.56%
	2	5.08	.0258	0.25	14.630	.0625	.401	
	3	5.08	.0309	0.25	13.908	.0625	.419	
	4	5.08	.0345	0.25	13.467	.0625	.431	
5020	1	5.08	0.216	0.25	6.130	.0625	0.682	7.6%
	2	5.08	.054	0.25	11.675	.0625	.482	
	3	5.08	.050	0.25	11.983	.0625	.473	
	4	5.08	.057	0.25	11.459	.0625	.488	

*Product determined from equation (2).

Table 12. Comparison of the Penetrations of $^{131}\text{ICH}_3$ for the same Carbon Weathered in Mode 1 and Mode 2 (see Section 3.5)

Weathered Layer	Depth (cm)	Pene- tration Fraction	τ (sec)	k_v	τ (sec)	$e^{-k_v\tau}$	Penetration Calc Obsvd (%) (%)
Test 5030 (Mode 1, 90% RH)							
1	5.08	.163	0.25	7.256	.0625	.6354	13.6
2	5.08	.132	0.25	8.100	.0625	.6028	
3	5.08	.152	0.25	7.535	.0625	.6244	
4	5.08	.107	0.25	8.940	.0625	.5719	
Test 5132 (Mode 2)							
1,2,3,4	5.08	.137	0.25				13.7
Test 5036 (Mode 1, 70% RH)							
1	5.08	.127	0.25	8.254	.0625	.5970	6.3
2	5.08	.051	0.25	11.904	.0625	.475	
3	5.08	.073	0.25	10.469	.0625	.5198	
4	5.08	.034	0.25	13.526	.0625	.4293	
Test 5131							
1,2,3,4	5.08	.0612	0.25				6.12

NOTE: The two columns headed 1,2,3,4 signify that the test column was assembled with equal volumes of carbon from the four weathered layers and arranged in the same sequence.

The values for the penetration of $^{131}\text{ICH}_3$ after weathering in outdoor air at NRL are summarized in Table 13. These include all data for the different commercial test carbons at the specified exposure times and locations.

Table 13. Penetration of $^{131}\text{ICH}_3$ Through Weathered Carbons
Exposed to Unmodified Outdoor Air at NRL

Test	Period (Mos.)	% Penetrations				Calcd. 1,2,3,4	Observd. 1,2,3,4
		1	2	3	4		
NACAR 615							
5016	1	1.77	0.64	0.34	0.70	0.72	
5031	2	3.42	1.32	0.86	1.02	1.41	
5022	3	8.62	1.38	1.19	0.81	1.84	
5097	3						3.13 ± .03
5098	3						0.59 ± .01
5099	3						3.10 ± .049
5058	6	8.33	0.27	0.34	0.18	0.61	
5057	9						6.62 ± .20
5133	9.5						4.54 ± .11
5123	12						4.82 ± .19
NACAR 617							
5017	1	1.90	0.62	0.32	0.64	0.70	
5023	1	12.91			5.40		
BC 727							
5014	1	2.67	1.20	0.68	1.31	1.30	
5070	1						1.13
5081	1						0.92
5082	1						0.69
5083	1						0.83
5113	1						13.2
5121	1 +						3.31 ± .141
5124	1						0.81
5032	2	5.81	2.58	3.09	3.45	3.56	
5065	2	15.4	4.8	5.1	5.8	6.84	
5096	2						3.79 ± 0.16
5020	3	21.6	5.4	5.0	5.7	7.59	
5056	6	13.3	0.97	1.50	0.97	2.08	
5055	9						15.6 ± .227
5122	12						14.1 ± .33
5113	1						13.2 ± .068
5125	1						0.73 ± .03
5126	1						0.07 ± .004
5127	1						0.81 ± .03
5128	1						0.29 ± .012
5130	1						0.35 ± .04
5150	1						7.62 ± .06
5156	2						14.86 ± .08

(continued)

Table 13 (continued)

Test	Period (Mos.)	% Penetrations				Calcd. 1,2,3,4	Observd. 1,2,3,4
		1	2	3	4		
BC 717							
5084	1						
5013	1	0.83	0.44	1.68	0.92	0.87	
5010	1						0.67
5024	1	11.7	3.75	3.75	4.86	5.32	
5019	1	13.2	11.6	11.8	9.86	11.55	
2701 (American Air Filter)							
5039	1	5.95	3.9	2.6	1.75	3.21	
5040	1	4.38	2.8	1.75	1.11	2.21	
5061	3						0.287 ± .051
5118	6	66.2	13.0	2.96	0.79	6.7	
5120	9	82.5	31.2	2.31	1.27	9.3	
5134	9						21.45 ± .27
KITEG (Nuclear Consulting Svcs, Inc.)							
5042	1						0.73
5069	3						3.22 ± .09
5119	6						8.20 ± .04
5117	9	95.2	55.1	37.4	22.5	45	
Sutcliffe & Speakman							
5033	1	8.63			0.52		
5034	1	3.88	0.87	0.43	0.45	0.90	
5078	1						.05
5079	1						<.02
5080	1						.02
5093	1 +						.13 ± .02
5110	1						0.39
5063	3	1.93	.05	.13	.08	0.18	
5064	6						0.82 ± 0.12
5066	9						0.46 ± .02
MSA (463563)							
5015	1	4.03	1.86	3.61	2.06	2.73	
5021	1	15.5	8.0	8.81	8.39	9.78	
5060	3						0.659 ± .020
5059	6						2.44 ± .34%
5077	9	17.8	9.91	0.10	0.27	1.48	
5135	9						7.00 ± .06

Note: The two columns headed 1,2,3,4 signify that the test bed was assembled with equal volumes of carbon from the four weathered layers and arranged in the same sequence.

The penetration results for locations outside of NRL are summarized in Table 14. The correlation of penetrations with the existing contaminants and dew point variations requires that each exposure be treated on an individual basis. This will be done for typical cases but not for all exposure tests.

Table 14. Penetration of $^{131}\text{ICH}_3$ Through Carbons Weathered at Sites Outside NRL

Test	Carbon	Time (mos.)	Water Extract pH				Penetration 1,2,3,4 %
			1	2	3	4	
Argonne National Laboratory							
5137	BC 727	1.3	7.9	8.7	8.7	8.7	1.35
5139	BC 727	7	6.8	9.0	9.1	9.0	30.02 ± .41
5164	BC 727	4	6.3	8.2	8.2	8.0	2.17 ± .16
5138	G 615	1.3	8.8	9.2	9.2	9.2	1.97
5140	G 615	7	6.8	9.5	9.5	9.6	5.44 ± .18
5165	G 615	4	7.0	8.3	8.3	8.3	0.30 ± .05
5192	S & S	2.5	6.8	7.6	7.6	7.6	1.88 ± .19 2.19%
5207	S & S	5	4.5	7.1	7.2	7.3	2.34 ± .52
Simi Valley, Ventura Co., CA							
5141	BC 727	7	6.5	8.1	8.7	8.7	25.9 ± .36
5166	BC 727	4	6.9	8.7	8.7	8.7	15.16± .62
5142	G 615	7	8.5	8.9	9.4	9.5	8.98 ± .21
5167	G 615	4	8.0	9.1	9.2	9.2	0.25 ± .08
5195	S & S	2.5	6.4	7.3	7.4	7.3	5.97 ± .48 11.07
5208	S & S	5.0	3.8	5.5	6.3	6.6	24.4; 30.6
Three Mile Island							
5172	S & S	2	7.4	7.6	7.8	7.9	0.18 ± .02
5171	G 615	2	8.05	9.10	9.07	9.05	0.10 ± .06
5190	G 615	4	9.0	9.1	9.1	9.1	0.22 ± .07
5191	Nusorb-Q	4	9.0	9.1	9.1	9.1	0.01 ± .01

An overview of all exposures leads to the summary graph of Fig. 14 in which the penetration of $^{131}\text{ICH}_3$ (percent) is plotted as a function of the exposure duration (months). The values can be divided into three distinct patterns, each corresponding to a type of impregnation on the carbon. The commercial carbons for nuclear installations have three types of impregnation: (1) KI_x (i.e., $\text{KI} + x\text{I}_2$), (2) $\text{KI} + \text{TEDA}$, (3) TEDA or some other tertiary amine. The penetration of the carbons after weathering decreased in the order (1) to (2) to (3) under

the manifold conditions existing at the three exposure sites. It appears that the impregnation formulation of a carbon is a critical choice toward realizing high removal efficiency and long service life.

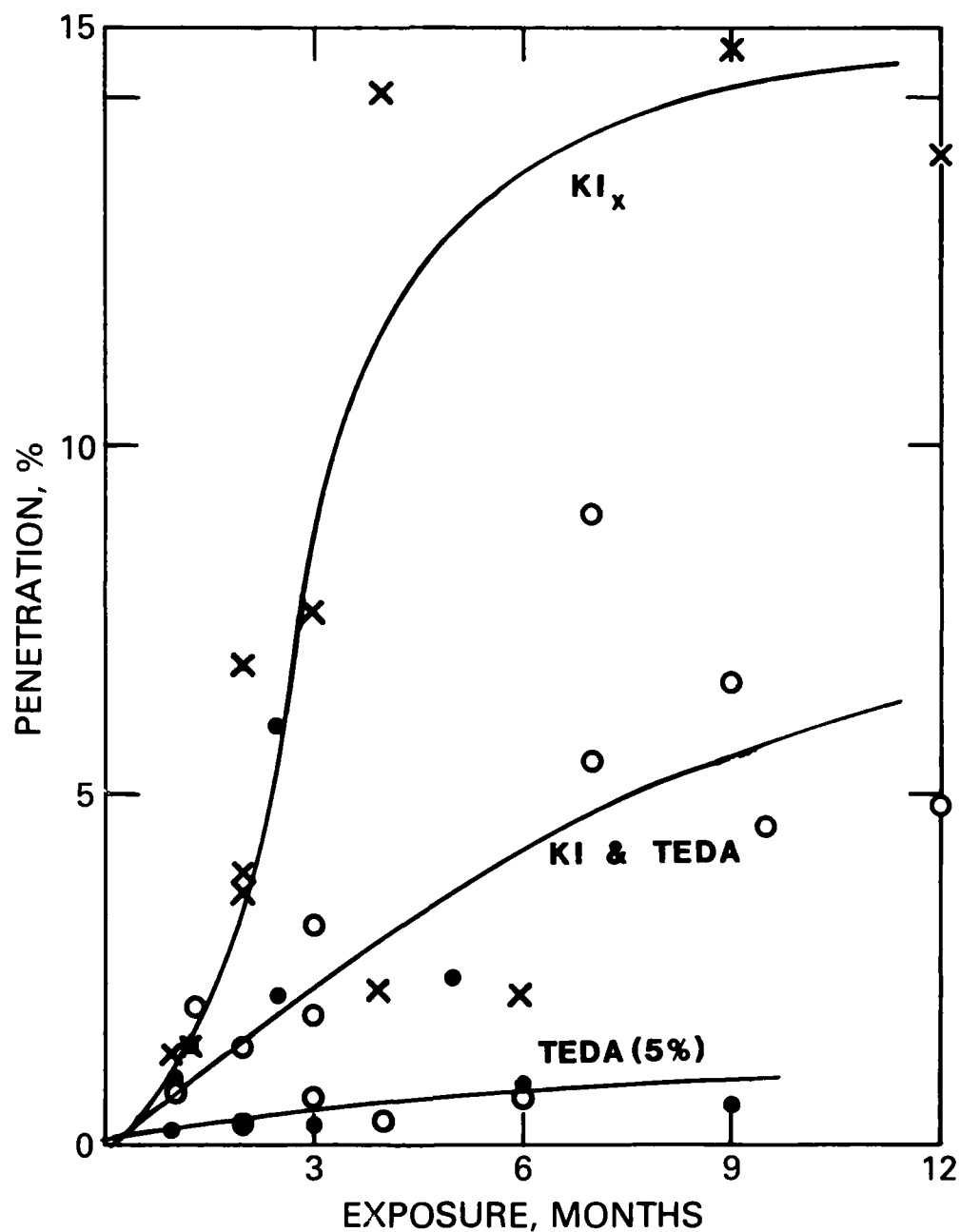


Figure 14. Penetrations of $^{131}\text{ICH}_3$ After Exposure to Outdoor Air at All Test Locations

IV. Laboratory Weathering Experimentations

The number of combinations of test gases and available carbons that warrant investigation is obviously very large. Care and consideration are needed to select the additional laboratory systems to study for possible correlation with outdoor exposures.

The sample container (Figure 7) used in the laboratory tests was the same as that in weathering with outdoor air. The air flow (100 L/min) passed in sequence (Figure 15) through 1) regulator-filter, 2) gas flow meter to indicate the flow and to integrate the total air flow, 3) particulate and carbon filter, 4) humidifier containing water at controlled temperature, 5) demister glass fiber, 6) air condenser (stainless steel tubing) to serve as an equilibrating column, 7a) side outlet from main flow to platinum temperature sensor, 7b) optical dew point hygrometer sensor, 8) stainless steel mixing chamber (4" diameter and 6" high) into which the contaminant is added to the air mixture through an injection port, 9) side outlet to analyzer for sampling inlet gases, 10) stainless steel carbon test container, 11) side outlet to analyzer for sampling exit gases, and 12) vent to hood. The carbon was dried prior to each experiment in order to determine the weight increase of the weathered material.

Several options are available in the test configuration for making the CH_3I -131 penetration tests. Since the volume of charcoal in each layer (4" dia. x 0.5" high) is equal to that required for a standard test (2" dia. x 2" high), the tests could be conducted in three ways as described previously:

(A) determine the penetration in each of the four individual layers of the weathered bed, requiring four determinations, (B) determine the penetration after taking one-fourth of each layer of the weathered bed and constructing a test bed in four layers in the same sequence of entrance-to-exit as in the weathering, and (C) determine the penetration of the weathered sample without removal of the carbon from the exposure configuration. The preferred procedure depends on the problem under investigation. Is a determination sought of the lifetime

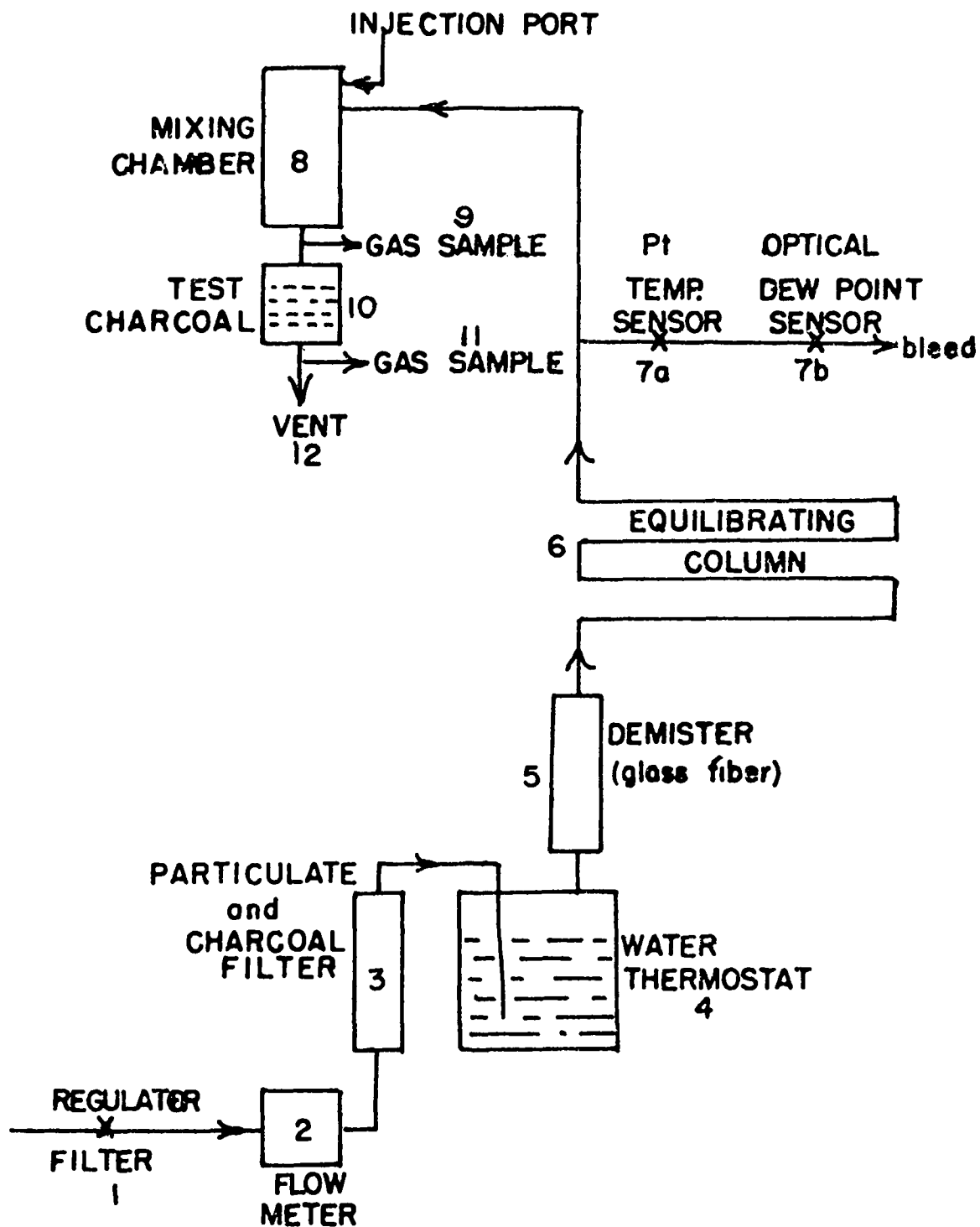


Figure 15. Flow Diagram of Laboratory Exposure Tests

of the exposed charcoal? Is information desired of the gradient within the bed and is a correlation desired of the results with the gradient brought about by weathering? These questions and others will be discussed after the presentation of the results.

The contaminant mixtures listed below were selected for laboratory measurements. In all cases, filtered compressed air was used at a linear flow of 40 ft/min. prior to the addition of controlled contaminants.

- air + water vapor at 50, 70 and 90% RH
- air + water vapor + sulphur dioxide
- air + water vapor + ozone
- air + water vapor + carbon monoxide
- air + water vapor + hexane vapor
- air + water vapor + carbon tetrachloride vapor
- air + water vapor + methylethylketone vapor
- air + water vapor + methyl alcohol vapor

4.1 Water Vapor Exposures

The controlled exposures of seven commercial carbons to air flows at three levels of relative humidity (50, 70, 90% RH) have been completed. The air flow was continuous at a flow rate of 100 L/min for 100 hours. The air was first humidified by bubbling the entire flow through water which was controlled at the desired temperature by a surrounding heat jacket. Humidities of 50, 70 and 90% RH were obtained by water temperatures of 11-12°C, 17-18°C, and 21-22°C, respectively. The residence time in the carbon bed was 0.25 sec. and the linear flow rate was 12.3 m/min. The total flow was thus 600 M³ and the total weight of water (calculated at 22°C) to which each carbon was exposed, was 0.97, 1.74, and 2.61 kg at 50, 70 and 90% RH, respectively. The exposure schedule of the carbons is given in Table 15. The temperature of the air-conditioned laboratory was kept in the range of 21 to 23°C. The relative humidity in each of the two independent exposure systems was monitored by a dew point hygrometer (General Easter, Series 1211 P Sensor) and the air temperature was measured simultaneously with a platinum resistance thermometer (General Eastern, 1212 P). The control, experimentally based on thermostated water supplies, realized an overall standard

deviation of 1-8% RH over the 100-hour laboratory exposure.

Table 15. Exposure Schedule of Test Carbons with Air-Water Vapor of Designated Constant Humidity for 100 hours

Carbon	Constant Humidity Maintained During Entire Exposure		
	50% RH	70% RH	90% RH
BC 727	4-8 Oct 1977 5053*	1-5 Aug 1977 5030*	15-19 Aug 1977 5036*
G 615	11-15 Oct 1977 5054*	8-12 Aug 1977 5035*	22-26 Aug 1977 5037*
MSA	24-28 Apr 1978 5073*	5-9 Jun 1978 5100*	8-12 May 1978 5086*
S & S	8-12 May 1978 5085*	7-11 Jun 1978 5101*	18-22 Apr 1978 5072*
2701	18-22 Apr 1978 5071*	12-16 Jun 1978 5102*	15-19 May 1978 5088*
G 617	15-19 May 1978 5087*	12-16 Jun 1978 5103*	24-28 Apr 1978 5074*
KITEG	1-5 May 1978 5075*	13-19 Jun 1978 5104*	1-5 May 1978 5076*

*Indicates the NRL Test Number

The inventory of water vapor introduced into the test carbons, given in Table 16, illustrates the capability of carbons to interact with water vapor. The total water vapor introduced in each experiment is between 5 and 10 kilograms; the quantity retained by the carbons in all instances is a small fraction (45-87 grams, or approximately 1% of the water vapor introduced).

The weight-gains (initially dried at 100°C) at different humidities at 21°C in the individual four layers of the seven carbons are given in Appendix 5. At 50% RH a distinct gradient was observed in the moisture gained by each of the four carbon layers; after the exposure of 100 hours, the weight gain by the entrance layer was significantly greater than by the exit layer. With air at 70 or 90% RH all layers showed essentially the same gain in weight. The lack of a gradient at 70% RH and above shows that at these levels of humidity, the water vapor is

Table 16. Water Vapor Inventory in Laboratory Weathering Experiments (21°C)

Run	Sample	RH %	Water Vapor g/m ³	Total Air Flow M ³	Total Water kg	Initial Dry Wgt. (g)	Wgt. (g)	Increase %
5025	BC727	70	12.9	690	8.90	180.2	84.0	46.6
5027	NACAR G615	70	12.9	450	5.81	228.4	63.9	28.0
5028	BC727	90	16.6	600	9.96	174.5	84.1	48.2
5029	NACAR G615	90	16.6	600	9.96	226.7	68.9	30.4
5030	BC727	70	12.9	600	7.74	182.7	83.0	45.4
5035	NACAR G615	70	12.9	600	7.74	226.7	64.9	28.6
5036	BC727	90	16.6	600	9.96	182.9	87.1	47.6
5037	NACAR G615	90	16.6	600	9.96	228.7	68.2	29.8
5038	NACAR G615	90	16.6	600	9.96	227.9	68.8	30.2
5043	BC727	90	16.6	318	5.28	181.1	83.5	46.1
5044	NACAR G615	90	16.6	648	10.76	226.0	66.7	29.5
5045	BC727	70	12.9	570	7.35	183.9	80.6	43.8
5046	NACAR G615	70	12.9	600	7.74	224.0	65.0	29.0
5053	BC727	50	9.2	600	5.52	183.7	47.4	25.8
5054	NACAR G615	50	9.2	600	5.52	224.0	44.8	20.0

sufficient to maintain a constant moisture content throughout the carbon bed. It may be noted that the weight increase at 90% RH was 30 wt.% or above for all test carbons under investigation; at 50% RH, the weight increase was below 26% or less in all cases.

The adsorption isotherm of water vapor by carbons is characterized by low adsorption up to about 40-50% RH, followed by a rapid rise and leveling off at progressively higher humidity. An example is the adsorption-desorption isotherm for NRL impregnated carbon No. 4284 (6) shown in Fig. 16. The three points

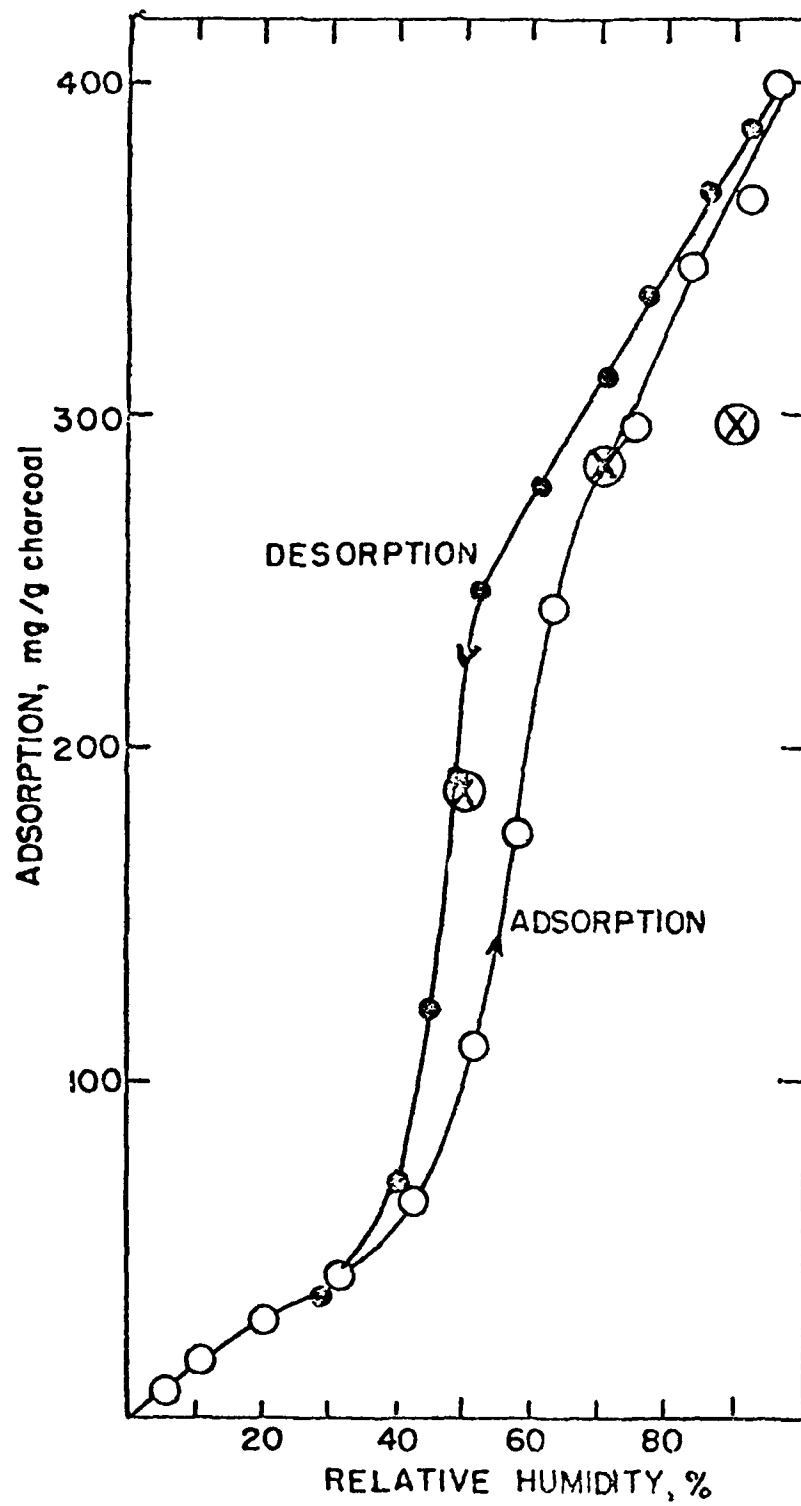


Figure 16. Adsorption-Desorption Isotherms for Water Vapor on NRL No. 4284 Impregnated Carbon, X = NACAR G-615

for NACAR G-615 were determined at 50, 70, and 90% RH. The similar behavior indicates a common property of the two carbons (NRL 4284 is a coal-base carbon impregnated in the laboratory with $\text{KIO}_3 + \text{KI} + \text{K}_3\text{PO}_4 + \text{hexamethylenetetraamine}$ and NACAR G-615 is a commercial coconut shell carbon impregnated with $\text{TEDA} + \text{KI}$). The weight increases followed a behavior consistent with the water adsorption isotherm of the carbon. The characteristic curvature of Fig. 16 accounts for the non-linearity of weight increase with relative pressure (see also Fig. 5 of NUREG/CR-0025). Consequently, the weight increases of all seven carbons in Appendix 5 were greatest at the highest humidity.

The shapes of the water vapor adsorption and desorption isotherms (Fig. 16) raise an interesting problem as to the behavior of carbon in a flow where a sequence of high and low humidity air are present. When the humidity of the air drops from 90 to 70% RH, the amount of water desorbed is not nearly as much as a drop from 70 to 50%. The removal, or the increase, of the water contained in carbon is thus dependent on actual meteorological conditions and any information on the subject would be valuable to a design for optimum trapping under variable magnitudes of relative humidity.

The weight increase of carbons exposed to humidified air-contaminant mixtures is dominated by the water vapor adsorption. The two carbons, BC 727 and NACAR G615, were humidified at 70 and 90% RH in the presence of SO_2 , O_3 or CO , and the weight gains, Table 17, show only small differences compared to water alone. The largest of the weight-gains were found for the exposures to SO_2 plus water vapor in three out of four exposures. The mobility of water vapor in porous solids depends on both the nature of the surface and the partial pressure of the water vapor. Flood (18) reported that the flow rate of water vapor through a porous activated carbon rod increased strongly above 50% RH. It can be anticipated, therefore, that the influence of water vapor on the penetration of methyl iodide-131 through a bed of carbon particles would be minimal below 50% RH. Indeed, Collins, Taylor and Taylor (12) showed this to be so for the penetration

Table 17. Weight Increase on the Exposure of the Test Carbons to Water Vapor With and Without Contaminant

NRL Test	% RH	Vapor	Wt. gain %	Mean (%)	Std. Deviation
BC 727					
5025	70	SO ₂ + H ₂ O	46.6	45.3	1.4
5030	70	H ₂ O	45.4		
5045	70	O ₃ + H ₂ O	43.8		
5028	90	SO ₂ + H ₂ O	48.2	47.3	1.1
5036	90	H ₂ O	47.6		
5043	90	O ₃ + H ₂ O	46.1		
NACAR G 615					
5027	70	SO ₂ + H ₂ O	28.0	28.5	0.5
5035	70	H ₂ O	28.6		
5046	70	O ₃ + H ₂ O	29.0		
5029	90	SO ₂ + H ₂ O	30.4	30.0	0.4
5037	90	H ₂ O	29.8		
5038	90	CO + H ₂ O	30.2		
5044	90	O ₃ + H ₂ O	29.5		

of methyl iodide using the 207B Sutcliffe and Speakman carbon impregnated with KI. The weight gains of the BC 727 samples exceeded the gains by NACAR G-615 by an amount between 15 and 20 g at 70 and 90% RH, although the BET surface areas of the carbons are approximately equal. The differences in weight gains may be attributable to the base carbons and the impregnations.

4.12 Exposures to Two Sequential Air Flows of Different Relative Humidity

Since the actual relative humidity of an air flow is never constant during an exposure to outside air, it would be useful to know how rapidly a carbon filter responds to air flows of different relative humidity. The laboratory exposure-schedule detailed in Table 18 was carried out in which the 100-hour exposure was replaced by two 50-hour periods. Each of two

carbons (G 615 and BC 727) was exposed in the following sequences of relative humidity: 50 → 90, 90 → 50, and 90 → dry air (dew point < 2°F).

Table 18. Exposure Schedule of Test Carbons to Air-Water Vapor at Two Levels of Relative Humidity (each 50 hours)

NRL Test	Carbon	First Exposure		Second Exposure	
		Date	% RH	Date	% RH
5089	G 615	22-24 May 78	50	24-26 May 78	90
5090	G 615	22-24 May 78	90	24-26 May 78	50
5108	G 615	3-5 July 78	90	5-7 July 78	dry air
5106	BC 727	26-28 Jun 78	50	28-30 Jun 78	90
5107	BC 727	26-28 Jun 78	90	28-30 Jun 78	50
5109	BC 727	3-5 July 78	90	5-7 July 78	dry air

The quantity of water retained by a test carbon at a given relative humidity is greater on the desorption than on the adsorption branch of the isotherm. This hysteresis is reproducible only under the steady state conditions reached in static systems. In flow systems pertinent to the present studies, the rates of adsorption and desorption that modify the weight-gain and weight-loss behavior depends on the duration of the exposure. Deitz and Blachly (19) showed that the largest weight-gains were obtained within the first ten hours and increased only slowly after 50 hours. The present results indicate that the highest relative humidity of a two-stage exposure may be the controlling factor in the weight-gain observed. These results are plotted in Fig. 17 where an arrow indicates the direction of the mass flow of water vapor. The change from 90% RH to 50% RH or the change from 50% RH to 90% RH yields approximately the same weight-gain of adsorbed water. However, the change from 90% RH to 0.8% RH does result in almost complete water removal. This example demonstrates the need to use low humidity air to dry carbons which have been exposed to air flows of high relative humidity.

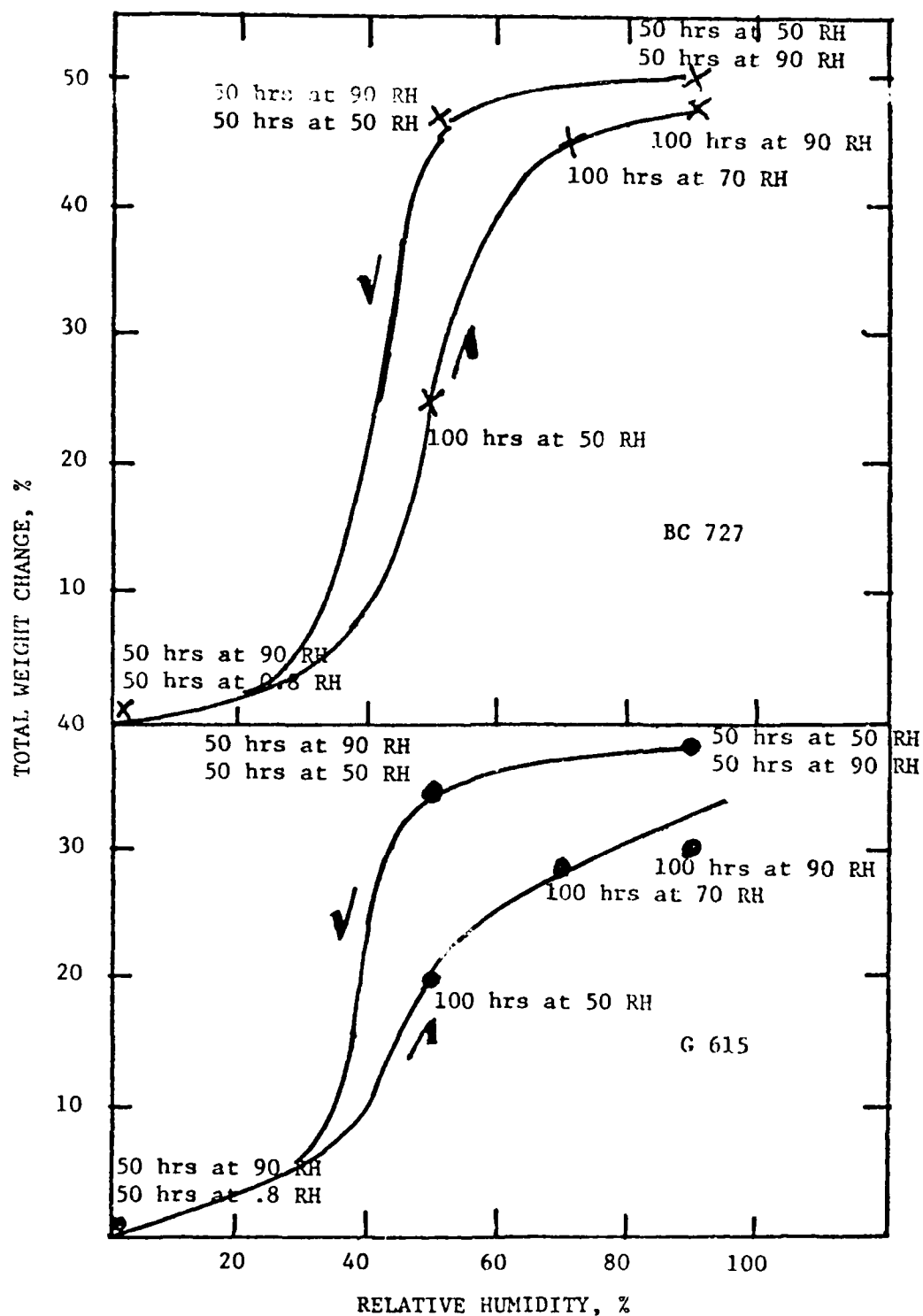


Figure 17. Exposures to Two Sequential Air Flows of Different Relative Humidity

The data (Figure 17) show that the carbons exposed to the sequence of 50 hours of air at 50% RH followed by 50 hours at 90% RH gains more weight than an exposure of 100 hours of air at 90% RH. This is a significant observation, but one that is difficult to interpret. The gas phase viscosity of water vapor at 20°C is almost half that of air and this can be a factor in the mass transport of water vapor into the fine porosity of the activated carbons. However, in order to explain the sequence of the above weight-gains, it is necessary to consider the basic adsorption process of water vapor on carbons and the mobility of the adsorbed water layer. A further discussion is beyond the scope of this investigation.

4.2 Ozone

The ozone was generated by an electrical discharge in a flow of dry oxygen through the annular space between two glass cylinders using electrodes external to the gas flow. The power source was a high voltage transformer (~10,000 V) and a constant voltage (105 V) was maintained on the primary. The ozone-oxygen mixture passed through a quartz cell (10 mm deep) located in a Beckman DU Spectrophotometer. The absorption band maximum of ozone at 2550 Å with an extinction coefficient of 3024 L/mole-cm was used to determine the ozone concentration (moles/L) and the results converted to $\mu\text{g}/\text{m}^3$. The ozone-oxygen mixture passed through a rotometer and was directed to the mixing chamber (Fig. 15), where it was diluted with the humidified air flow. The absorbency of the ozone-oxygen mixture from the generator proved to be inversely proportional to the rate of flow of oxygen into the electric discharge. The data are given in Table 19.

The inventory of the ozone insult is summarized in Table 19. No ozone was detected in the effluent air for all tests with these two carbons; the lowest concentration that could be detected was 0.007 ppm. Previous work in the laboratory (20) showed that the weight increase of a carbon exposed to ozone was equal to one-third of the weight of ozone introduced. Assuming

Table 19. Performance of the Laboratory Ozone Generator

Run	Absorbance		O2 Flow		Total Air Flow		Ozone ppm
	Mean	Standard Deviation	Standard		Standard		
			Mean (cc/min)	Deviation	Mean (L/min)	Deviation	
5043	0.61	0.09	55.0	4.0	98.8	1.0	2.51
5044	0.66	0.10	52.2	7.2	99.5	0.6	2.56
5045	0.90	0.13	40.8	2.8	100.3	0.34	2.71
5046	1.02	0.12	35.9	3.5	99.9	0.53	2.71

that all the chemical interaction is in the first layer of carbon, the change in weight due to the ozone was 1.2 and 2.4 weight percent for carbon BC 727, and 2.1 and 2.1 wt. % for carbon NACAR G-615. The pH of the water extracts of the entrance layers diminished somewhat for BC 727, as shown in Table 20, relative to the new carbon.

Table 20. Total Ozone Insult in Laboratory Experiments

Carbon	5043	5044	5045	5046
	BC 727	NACAR G-615	BC 727	NACAR G-615
RII %	90	90	70	70
volume air (M ³)	318	648	570	600
ozone (ppm)	2.51	2.56	2.71	2.71
ozone, standard deviation	0.37	0.39	0.39	0.32
total ozone (g)	1.7	3.5	3.3	3.5
weight carbon, entrance layer (g)	45.3	56.5	46.0	56.0
% increase in weight of entrance layer	1.2	2.1	2.4	2.1
pH (entrance layer)	8.6	9.3	8.7	9.7
pH, new carbon	9.5	9.8	9.5	9.8

4.3 Sulfur Dioxide

The source of the sulfur dioxide was a pressure tank (Linde Specialty Products Division, Union Carbide) containing 0.11 volume percent SO_2 in nitrogen. A flow of 50 ml/min was directed into the mixing chamber and with an air flow maintained at 100 L/min, the insult to the carbon was 0.55 ppm (V/V). The concentrations of SO_2 at the entrance and exit of the test carbon were measured with the Meloy Total Sulfur Analyzer (SA 160-2) and Calibration Source (CS 10-2). These instruments are EPA standard references for flame photometric determinations. A 3-pen recorder was used to record simultaneously the dew point, the temperature, and total sulfur data.

The inventory of the sulfur dioxide insult is summarized in Table 21. For the two carbons tested, no trace of sulfur dioxide was detected in the effluents (detection limit = 0.005 ppm). The value given for the concentration was the time average over the entire weathering exposure (100 hrs) and the total sulfur dioxide was the product of the total flow and average concentration. The entrance layer of the carbon bed appeared to retain the major fraction of the sulfur dioxide, since the pH of the water extracts of this layer was distinctly more acidic than the subsequent layers. These data are contained in Table 21. Knowing the final weight of the carbon and assuming the total sulfur dioxide to be retained in the entrance layer, the calculated concentration of SO_2 in carbon BC 727 was 1.8 and 1.8 wt. % and in carbon NACAR G-615, it was 1.0 and 1.4 wt. % at 70 and 90% RH, respectively.

The quantities of sulfur dioxide introduced in tests 5027 and 5029 with the same carbon (G-615) were 0.56g and 0.79g, respectively. The corresponding pH of the entrance layers was 6.4 and 3.5, in direct consequence of the amounts of sulfur dioxide introduced. In contrast, the almost equal quantities of sulfur dioxide introduced in tests 5025 and 5028 (BC 727) yielded pH values of same magnitude (2.7 and 3.2). Since the pH values of the layers 2, 3, and 4 were 9 or above in all tests with sulfur dioxide (Table 21), it is suggested that the quantity of sulfur dioxide required to penetrate the first layer is somewhat

in excess of 0.80 g.

Table 21. Total Sulfur Dioxide Insult in Laboratory Experiments

Carbon	Test Number			
	5025 BC 727	5027 NACAR G-615	5028 BC 727	5029 NACAR G-615
RH %	70	70	90	90
volume air (M ³)	690	450	600	600
sulfur dioxide ppm (mean)	0.45	0.49	0.51	0.51
sulfur dioxide standard deviation	0.024	0.016	0.042	0.016
total sulfur dioxide (g)	0.80	0.56	0.78	0.79
weight carbon, en- trance layer (g)	43.88	56.47	44.27	56.71
wt.% sulfur dioxide in entrance layer	1.82	1.0	1.8	1.4
pH (entrance layer)	2.7	6.4	3.2	3.5

4.4 Carbon Monoxide

The source of the carbon monoxide was a pressure tank containing 1.2 volume percent CO in air. The dosing procedure was similar to that used for SO₂. The concentration of CO was determined in a known aliquot drawn from the air stream through a Beckman Carbon Monoxide Analyzer, the sensitivity being approximately 0.1 ppm. Variations of CO in the air source could be detected and due allowances made in calculating the integrated insult to the carbon.

The weathering experiment, NRL 5038, was made with carbon monoxide and NACAR G-615 in an air flow at 90% RH. The concentration of CO entering and leaving the carbon did not differ significantly. The mean and standard deviation of the concentrations over the 100 hours (09:10 30 August to 13:10 3 September) are given in Table 22. No change in the pH of the water extract was observed relative to that of the starting material.

Table 22. Concentrations of Carbon Monoxide Used in NRL 5038

	CO Concentration (ppm)	CO (ppm)
	mean	standard deviation
Inlet	4.5	1.4
Outlet	4.0	0.9

4.5 Organic Vapors in Humidified Air

The adverse influence of extraneous organic materials on methyl iodide penetration was reported several years ago by Bennett and Strege (21). Assuming a concentration of 5 ppm hexane, for example, and a flow of 100 L/min, the amount of hydrocarbon entering a 2-inch carbon test filter in 100 hours is 10.3 g. Depending on the density of the carbon, this quantity corresponds to a potential loading of 5 to 7 wt.% of the carbon. In preliminary experiments at NRL, a number of test carbons were allowed to adsorb a known quantity and type of hydrocarbon and the penetrations of methyl iodide-131 were then determined. In one series, the carbons were prehumidified (16 hrs. exposure to air of 95% RH at a flow of 25 L/min) and in the second series, the same carbons were not prehumidified. The objective was to observe the magnitude of the synergistic influence of water vapor and hydrocarbon on the trapping efficiency. The results (Table 23) give the methyl iodide-131 trapping efficiencies of four carbons with and without prehumidification after the hydrocarbon contamination, and also the results after exposure to water vapor alone. Without prehumidification, there is an increase in penetration relative to the original carbon, but the efficiencies remain within suggested acceptable performance requirements for nuclear grade carbons. After the prehumidification, the penetration was markedly increased.

All of the combinations of carbons and pollutants in Table 23 were not studied since the results already demonstrated the synergistic influence of water vapor and hydrocarbon. For

example, the penetration for BC 727 was 4.8% for water vapor alone and 0.63% for 2% $C_{14}H_{30}$ alone, but 9.5% for both water vapor and 2% $C_{14}H_{30}$. Also, the penetration for MSA 463563 was 2.5% for water vapor alone and 1.01% for 2% $C_{14}H_{30}$ alone, but 7.5% for both water vapor and 2% $C_{14}H_{30}$. Additional weathering exposures (Table 24) involve the insult mixture of organic vapor and 95% RH air flowing continuously into the carbon bed. The weathering was followed by the determination of methyl iodide-131 penetration. The compounds selected include n-hexane, methanol, carbon tetrachloride, and methylethylketone.

Table 23. Influence of Prehumidification on Trapping Efficiency after Hydrocarbon Contamination

Carbon	*Prehumidification	BC 717	BC 727	MSA 463563	G 615
Orig.	No	.05	.014	0.13	0.05
Orig.	Yes	1.0	4.8	2.5	0.27
+10% Octane	No			0.37	
	Yes			9.2	
+10% $C_{14}H_{30}$	No	1.2	0.33	0.80	
	Yes	5.3	15.6	15.9	
+2% $C_{14}H_{30}$	No	0.63	0.63	1.01	0.18
	Yes	8.8	9.5	7.5	1.5
+0.2% $C_{14}H_{30}$	No				0.09
	Yes				0.81

* Prehumidification: 16 hrs., 25 l./min, 95% RH

Some pertinent data helpful in the preparation of the vapor mixtures at the desired concentrations are given below:

	MW	d(g/cc)	bp°C	Temp at 10 torr (°C)
n-hexane	86.17	0.659	68.7	-25.0
methanol	32.04	0.792	64.7	-16.2
carbon tetrachloride	153.8	1.594	76.8	-19.6
methylethylketone	72.10	0.805	79.6	-

To prepare the air-vapor mixtures, a small glass trap containing the organic liquid of interest was thermostated and a small controlled flow of air was introduced using all-glass or Teflon tubulation. This flow was injected into the main air flow (100 L/min) which passed through the mixing chamber (Fig. 15). A small aliquot of the effluent from the mixing chamber was directed through the sampling loop of a 5710 Hewlett Packard Chromatograph having a FID detector. The air flow through the organic liquid was then adjusted in order to reach the desired concentration of the organic vapor in the combined air flow. Calibrated permeation tubes were used in these experiments as standards for calibrating the gas chromatograph (see Appendix 6).

Prior to placing a test carbon sample in the laboratory weathering apparatus, the air flow was adjusted to 100 L/min and the desired concentration of contaminant was obtained at the regulated relative humidity. After the system reached a steady state, the container of carbon was placed in position and the air flow readjusted to 100 L/min to compensate for the resistance to flow through the carbon. No further attention was required except to add water to the humidifying bath about twice in each 24 hours and to renew the level of organic liquid in the glass trap.

The control realized is shown by the examples for the low-level insult of carbon tetrachloride (NRL Tests 5180 and 5181, see Table 24). Over the 100-hour period, 41 chromatographic data points were obtained. For NRL 5180 the mean concentration was 2.4 ppm carbon tetrachloride with a standard deviation of 0.35 ppm; for NRL 5181 with an equal number of data points, the mean concentration was 3.0 ppm with a standard deviation of 0.72. The laboratory exposures were on a continuous basis.

Table 24. Exposure of Impregnated Carbons to Organic Vapors at Constant Relative Humidity for 100 hrs. at an Air Flow of 100 L/min.

NRL Test	Nuclear Carbon	Organic Vapor	Time	Wt. %	pH	Penetration, % CH ₃ I-131
5199	727	MeOH	4-8 March '80			
1				30.4	8.17	
2				30.5	7.95	
3				30.5	8.17	
4				30.6	8.17	2.12±1.3
5198	615	MeOH	4-8 March			
1				28.3	9.30	
2				28.0	9.30	
3				26.9	9.18	
4				26.0	9.3	0.15±.03
5189	615	MEK	19-23 Feb.			
1				31.1	7.16	
2				31.0	7.14	
3				30.9	7.07	
4				30.4	7.15	1.47±.24
5188	727	MEK	19-23 Feb.			
1				32.6	7.0	
2				32.7	7.1	
3				32.7	7.1	
4				32.9	7.1	0.09±.05
5185	615	MEK	11-15 Feb.			
1				31.3	7.2	
2				31.3	7.3	
3				31.3	7.4	
4				30.8	7.7	0.76±.14
5184	727	MEK	11-15 Feb.			
1				35.2	7.2	
2				35.2	7.3	
3				35.3	7.3	
4				35.4	7.4	12.8±.97
5183	615	CCl ₄	4-8 Feb.			
1				30.4	9.0	
2				30.4	8.9	
3				30.2	9.0	
4				30.4	9.1	1.84

(continued)

Table 24.(continued)

NRL Test	Nuclear Carbon	Organic Vapor	Time	Wt. %	pH	Penetration, % CH ₃ I-131
5182	727	CCl ₄	4-8 Feb.			
1				34.2	8.2	
2				33.8	8.4	
3				33.6	8.3	
4				33.4	8.0	6.22±.25
5181	615	CCl ₄	28 Jan-1 Feb.			
1				34.3	9.1	
2				35.6	9.0	
3				36.1	9.0	
4				35.5	9.0	2.08±
5180	727	CCl ₄	28 Jan-1 Feb.			
1				39.72	8.6	
2				39.12	8.7	
3				38.84	8.5	
4				38.70	8.6	1.83±
5179	615	Hex	21-25 Jan.			
1				35.1	9.0	
2				35.1	9.1	
3				34.9	9.0	
4				34.4	9.0	0.21±.05
5178	727	Hex	21-25 Jan.			
1				35.9	8.51	
2				35.9	8.58	
3				36.1	8.6	
4				36.4	8.5	8.72
5174	727	Hex	14-18 Jan.			
1				38.5	9.2	
2				38.5	9.2	
3				38.2	9.2	
4				38.2	9.2	5.77
5173	615	Hex	14-18 Jan.			
1				28.7	9.6	
2				28.6	9.5	
3				28.6	9.6	
4				29.7	9.5	1.35

MeOH = methyl alcohol

MEK = methylethylketone

CCl₄ = carbon tetrachloride

Hex = n-hexane

4.6 Penetration Results

The results are examined from the point of view of two dynamic sequential adsorption processes. First, the weathering action takes place with the penetration of the contaminant into the four layers of carbon to an extent which depends on the concentration of the contaminant, residence time, the reaction rate constant, the linear air velocity, and geometry of the carbon bed. Second, the change produced in the properties of the carbon is then measured by the penetration of the test gas, methyl iodide, in accordance with the specified parameters of the ASTM qualification tests. In the weathering process, the influent concentration of water vapor, ozone, sulfur dioxide, carbon monoxide, or organic vapor was held constant; in the second process, the test mixture of methyl iodide-131 + water vapor was constant, and then followed by an air purge. During the weathering stage, no trace of ozone or sulfur dioxide was detected in the exit gases during the test period (100 hrs) and no change in CO concentration was detected in passing through the carbon. This indicates the high adsorption capacity of the carbon for ozone and sulfur dioxide, and no detectable adsorption for carbon monoxide.

Tables 25 and 26 summarize the results for the penetration of methyl iodide-131 in the laboratory weathering experiments. These penetration tests were conducted without prehumidification and the methyl iodide penetration was determined for each of the four half-inch layers of the weathered bed. It is obvious that the entrance layers have been influenced to the greatest degree by the insult gases (excepting CO) and the penetration of methyl iodide was always greater therein than in the subsequent layers. The weight gain of each layer and the pH of the water extract were determined immediately after the weathering. In most cases, the additional tests were made within two weeks after weathering, but in no case were they delayed for more than two months. The carbon from each layer was stored in a glass container with a screw cap, using a thin Mylar film

Table 25. Penetration of Methyl Iodide-131 in Laboratory Weathering with Water Vapor and Water Vapor + Sulfur Dioxide

	Test Number				Test Number			
	5030	5035	5036	5037	5025	5027	5028	5029
Insult	Water Vapor				SO ₂ + water vapor			
carbon	BC727	G615	BC727	G615	BC727	G615	BC727	G615
% RH	70	70	90	90	70	70	90	90
time (hrs)	100	100	100	100	115	75	100	100
Volume (m ³)	600	600	600	600	690	450	600	600
pH, entrance	7.7	9.0	8.2	9.5	2.7	6.4	3.2	3.5
second	9.2	9.5	9.1	9.5	9.2	9.6	9.4	9.4
third	9.1	9.6	9.1	9.4	9.0	9.7	9.5	9.3
fourth	8.8	9.6	9.2	8.8	9.0	9.8	9.5	9.5
*P(CH ₃ I) entrance	16.3	2.4	12.7	2.0	37.5	7.2	66.0	16.0
second	13.2	1.6	5.1	nd	11.2	1.6	nd	nd
third	15.2	1.6	7.3	nd	9.9	1.2	nd	nd
fourth	10.7	1.8	3.4	2.1	10.9	2.1	17.0	2.6
wt. increase	45.4	28.6	47.7	29.8	48.6	27.7	50.4	32.0
second	45.3	28.5	47.7	30.0	45.9	27.9	47.6	30.1
third	45.5	28.6	47.5	29.7	46.1	27.9	47.5	29.9
fourth	45.3	28.6	47.3	29.9	45.9	28.6	47.4	29.5

*P(CH₃I) = Percent Penetration of Methyl Iodide; nd = not determined

	<u>BC 727</u>	<u>NACAR G-615</u>
initial pH	9.5	9.8
initial penetration (no prehumidification)	0.01	0.05

Table 26. Penetration of Methyl Iodide-131 in Laboratory Weathering of Nuclear Carbons with Water Vapor + Ozone and Water Vapor + Carbon Monoxide

	5043	Test 5044	5045	5046	Test 5038
Insult	O ₃ + water vapor				CO + water vapor
Carbon	BC 727	G-615	BC 727	G-615	G-615
% RH	90	90	70	70	90
time (hr)	53	108	95	100	100
Vol (m ³)	318	648	570	600	600
pH					
entrance	8.6	9.3	8.7	9.7	9.5
second	9.4	9.8	9.5	9.9	9.7
third	9.4	9.8	9.6	9.9	9.6
fourth	9.5	9.8	9.6	9.9	9.6
*P(CH ₃ I-131)					
entrance	19.0	3.1	18.3	1.9	3.0
second	11.7	1.4	7.7	nd	1.5
third	13.9	3.0	11.0	nd	1.8
fourth	21.5	0.7	12.2	2.9	1.2
wt. % increase					
entrance	46.1	29.6	44.1	29.0	30.6
second	46.3	29.5	44.0	29.0	30.9
third	46.2	29.4	43.4	28.5	29.7
fourth	46.0	29.5	43.8	29.3	29.6

*P(CH₃I-131) = Percent Penetration of Methyl Iodide-131;
nd = not determined

between the cap and container. The time interval between exposure and the penetration determination has been recorded for possible future correlation.

Judged by the penetration of methyl iodide-131, three out of the four contaminant mixtures have been found to degrade the two carbons seriously in a relatively short time. The sulfur dioxide + water vapor and the ozone + water vapor mixtures exceed the influence of water vapor alone. The exposures to the mixtures of ozone or sulfur dioxide with water vapor resulted in a large adsorption of water vapor within all four layers of a test, but the ozone or sulfur dioxide interaction was confined to the first layer. This is due, in part, to the large difference in concentration of the two components introduced; ozone about 2.5 ppm, sulfur dioxide 0.5 ppm, and water vapor about 200,000 ppm. As shown in Tables 22 and 23, the pH of the water extracts of the first layer only were reduced and the methyl iodide-131 penetrations were correspondingly increased. This is not strictly speaking, a synergistic effect; the latter would require the total to be greater than the sum of the two effects taken independently. It does demonstrate that humidified carbons present strong adsorption sites for the two contaminants considered.

Carbon monoxide appears indifferent and does not influence the methyl iodide-131 penetration. It must be kept in mind that the laboratory weathering is conducted with constant influent concentration of contaminant. In contrast, the carbons weathered in unmodified outdoor air are subject to continuous changes in contaminant concentration (13, 22) and the insult may be alleviated in some situations. However, the potential for degradation of the carbon efficiency by the contaminants of the outdoor air is ever present.

The two commercial carbons, BC 727 and NACAR G-615, have shown different behaviors in the weathering experiments to date. These are two of the six coconut-base carbons studied and a better judgment can be made when the impregnation is included. There is a different impregnation on carbon BC 727 (KI_x) than on carbon NACAR G-615 (KI + TEDA) and the response to the chemical

reactions of weathering can differ. The migration among the carbon particles of certain components of the impregnation depends in part on the volume of the air flow and the mobility of these compounds. A formulation containing triethylenediamine (TEDA) may slowly lose this component by its volatility (the vapor pressure of TEDA is 2.9 torr at 50°C and 0.6 torr at 25°C) and a formulation containing KI_x may lose iodine by decomposition into elemental I_2 . It is not known how the adsorbed impregnation on charcoal affects the slow volatility of TEDA into air + water vapor.

The methyl iodide-131 penetrations (Table 27) increased for all seven carbons with increase in the relative humidity of the air flow. The increase from 50 to 70% RH was greater than the increase from 70 to 90% RH. The differences among the different carbons, seen in Fig. 18, vary to some extent, but it is important to remember that these measurements are based on a single production sample (25 lbs.) of each type. The behavior of the S & S, 5% TEDA, according to these measurements, is outstanding for weathering in water vapor only. Mixtures of pollutants and water vapor will be discussed in another section.

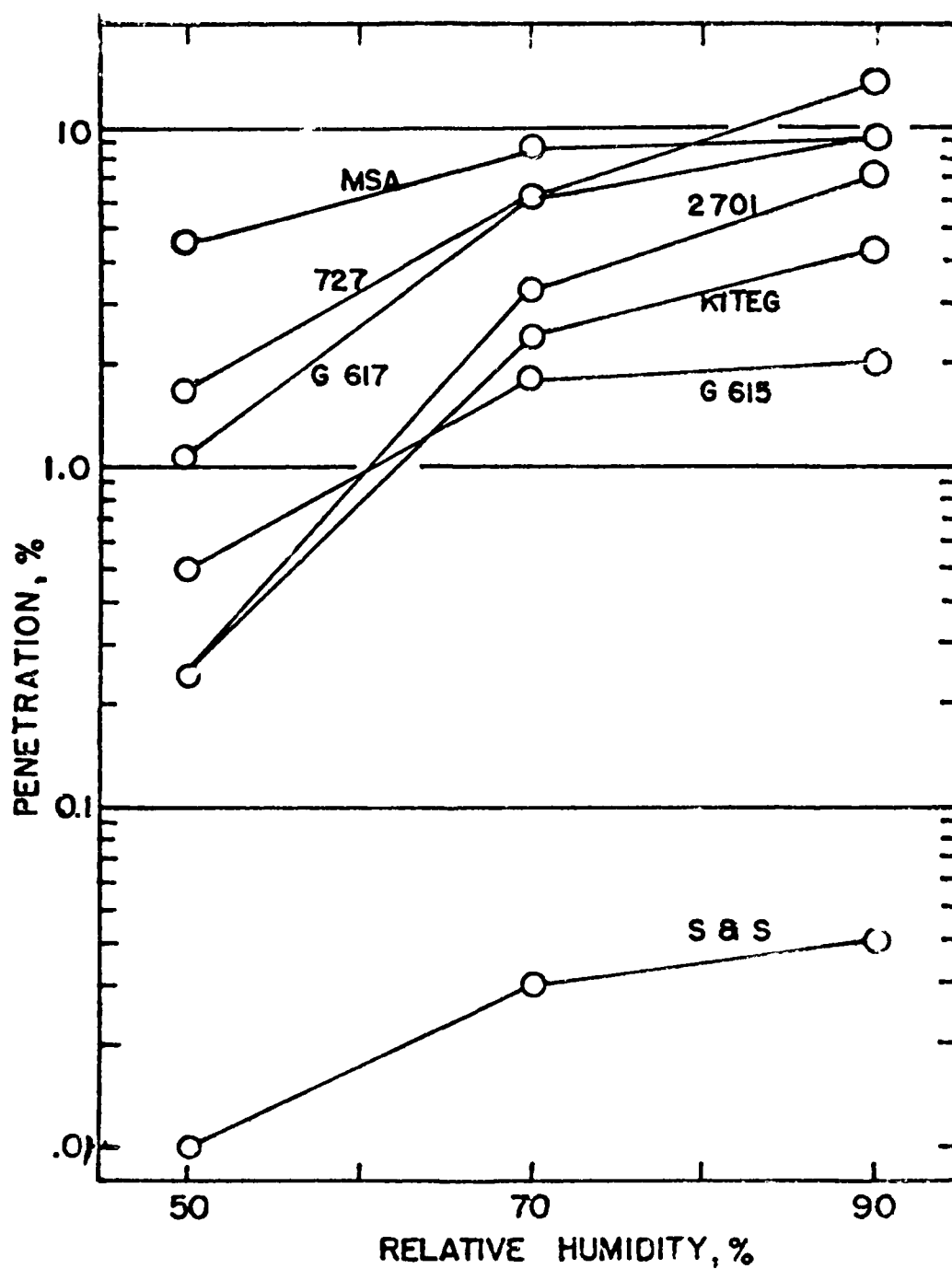


Figure 18. Methyl Iodide-131 Penetration for Carbons Weathered at Constant Relative Humidity (21-23°C) for 100 Hrs at 100 L/min (see Table 27).

Table 27. Results for Seven Commercial Carbons Exposed at Constant Relative Humidity for 100 hrs. at an Air Flow of 100 L/min.

Carbon	Relative Humidity %	pH (av)	Average of Weight Increase %	Methyl Iodide-131 Penetration %
BC 727	50	9.5	25.8	1.69
	70	8.7	45.4	6.3
	90	8.9	47.6	13.6
G 615	50	9.9	20.0	0.50
	70	9.4	28.6	1.8 ± .04
	90	9.3	29.9	2.0
MSA 463563	50	8.3	21.4	4.66 ± .09
	70	8.1	36.1	8.6 ± .09
	90	8.3	39.0	9.27 ± .06
S&S (5% TEDA)	50	8.4	15.4	<.01
	70	8.4	26.7	<.03
	90	8.7	31.9	.04 ± .01
AAF 2701	50	9.1	18.9	0.24 ± .02
	70	8.6	43.6	3.29 ± .04
	90	8.7	51.5	7.21 ± .05
G 617	50	9.4	20.3	1.10 ± .02
	70	9.2	57.4	6.20 ± .05
	90	9.6	61.5	9.10 ± .13
KITEG	50	7.7	18.6	0.25 ± .03
	70	7.7	29.1	2.45 ± .03
	90	7.7	40.0	4.37 ± .27

The general behavior of the above test carbons was found to be reproducible. For example, two samples of BC 727 were exposed in August 1977 and in October 1978 and the results are given in Table 28. The good reproducibility obtained for BC 727 may be due in part to the close control possible in laboratory weathering and to the good reproducibility of the carbon samples

Table 28. Reproducibility of Laboratory Weathering (BC 727)

Test	Exposure	RH%	CH ₃ I-131 % Penetration
5030	1-5 Aug 1977	70	6.3
5131	16-20 Oct 1978	70	6.12 ± .076
5036	15-19 Aug 1977	90	13.6
5132	16-20 Oct 1978	90	13.7 ± .127

withdrawn from the master stock supply.

The results for the carbon exposures to air flows of two sequential levels of relative humidity (see Fig. 17) are summarized in Table 29 and the observed CH_3I -131 penetration is shown to be dependent on the sequence of the exposure. These results are shown graphically in Fig. 19. Of particular interest is the fact that the observed penetration of methyl I-131 after 100 hours in air of 90% RH is more than twice that after 50 hours of 50% RH plus 50 hours at 90% RH. Previously in connection with Figure 17 (page 52) the weight gains were approximately equal for both cases with 100 hours at 90% RH having the lower weight gain. The greater penetration after 100 hours at 90% RH appears to be independent of weight-gain behavior. Moreover, the results for penetration after 50 hours at 90% RH + 50 hours at 50% RH are approximately the same as 50 hours at 50% RH + 50 hours at 90% RH. Apparently, only the exposure to air at 90% RH is the degrading factor.

Table 29. Results after Exposure at Two Sequential Levels of Relative Humidity (Total time 100 hrs)

Carbon	Exposure Time(hrs)	% RH	pH	Total Wt. Change %	Penetration %
G 615	50	50			
	50	90	9.5	38.8	0.66 ± .02
G 615	50	90			
	50	50	9.4	34.8	0.69 ± .06
G 615	50	90			
	50	dry air	9.3	0.84	0.06 ± .01
G 615	100	90	9.3	29.9	2.00
G 615	100	50	9.9	20.0	0.50
BC 727	50	50			
	50	90	9.2	50.1	5.88 ± .05
BC 727	50	90			
	50	50	9.0	46.9	3.95 ± .04
BC 727	50	90			
	50	dry air	8.9	0.78	1.02 ± .05
BC 727	100	90	8.9	47.6	13.6
BC 727	100	50	9.5	25.8	1.69

The penetration of methyl iodide-131 has also been studied by Deitz and Blachly (19) as a function of the duration of prehumidification (air at 25 L/min and 95% RH) and the penetration was found to increase with increased times of prehumidification. It required about 100 hours before the penetration leveled off; the penetration doubled on extending the prehumidification from 50 to 100 hours. The present results (Table 29) show a similar dependence on exposure time. The penetration after the 100-hr contact times are given, Fig. 19, for G 615 and BC 727. It is evident that the two additional exposures for each carbon that had received only 50 hours at 90% RH did not result in as much penetration. The increased penetration with increased times of prehumidification was quite unexpected when first observed in 1976 with experimental carbons, and it is important to note that the same effect is present for commercial carbons.

The exposure of the test carbons to two levels of relative humidity only approximates the great variability encountered in practice. The carbon in service is subjected to variable periods of high and low relative humidity; periods of dry air could be favorable to high trapping efficiency and periods of wet weather would steadily increase the moisture content and decrease efficiency. These preliminary results indicate that it could be advantageous to introduce a flow of air in dry weather to dehydrate effectively those filters which otherwise may not be in operation at that time.

Organic vapors in air mixtures without water vapor were added to one of the carbons to a level of 11 wt.%. The results are given in Table 30. The addition of 11 wt.% of these compounds did not degrade the carbon below the allowable performance requirements. However, based on the results previously presented in Table 24, unacceptable methyl iodide-131 penetration can result when a combined flow of water vapor and organic vapor is allowed to enter the test carbon for an appreciable length of time.

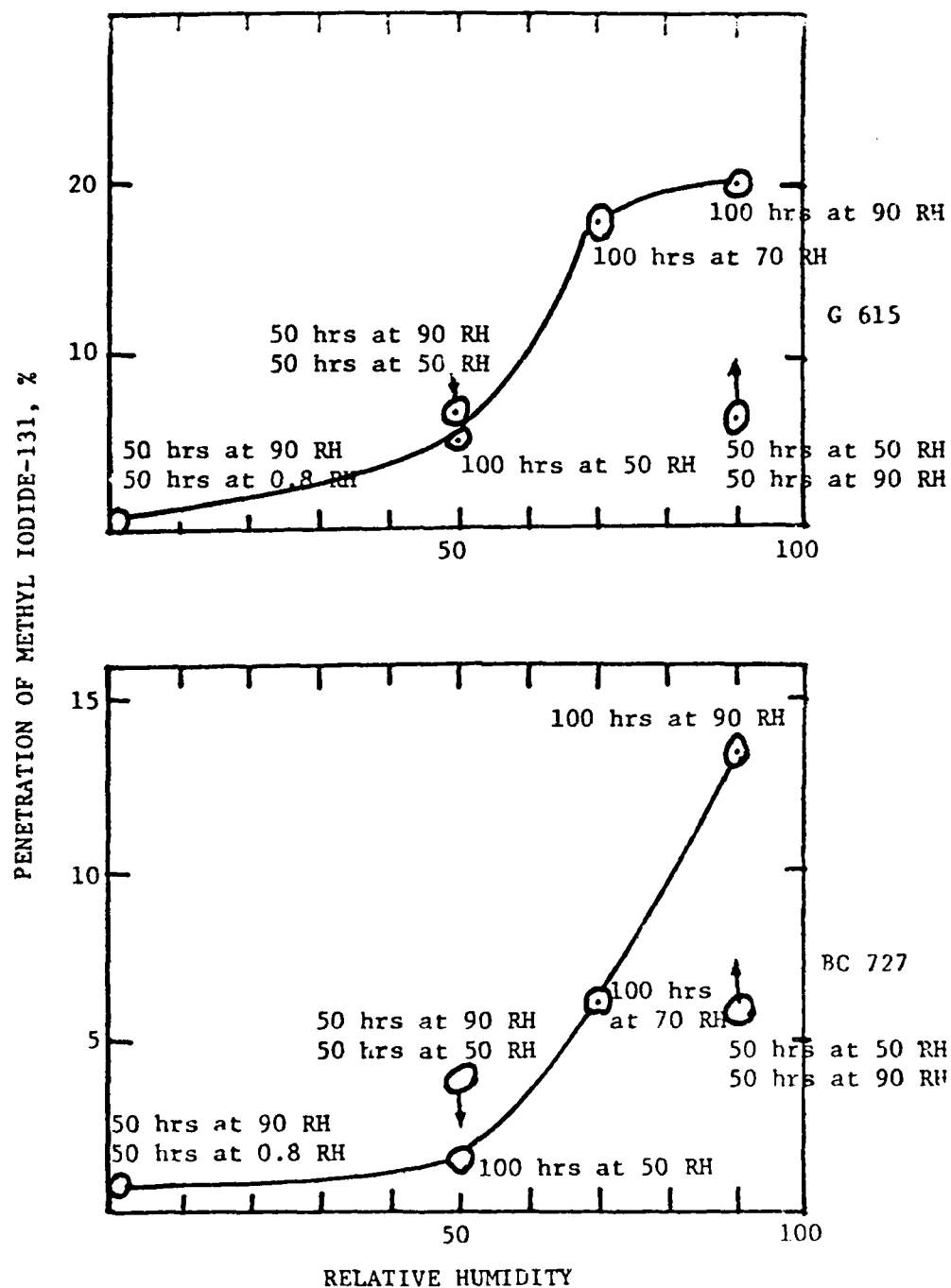


Figure 19. Penetration on Exposure to Sequential Changes in Relative Humidity

Table 30. Penetration of Methyl Iodide-131 After Contamination without the Presence of Water Vapor

Test	Carbon	Contaminant	CH ₃ I-131 Penetration
-	BC 727	None	0.014
5114	BC 727	Hexane	2.04 ± .04
5115	BC 727	Methanol	0.77 ± .05
5116	BC 727	Methyl Isobutyl Ketone	1.19 ± .10

V. Thermal and Chemical Analyses of Service-Weathered Carbons

5.1 Total Iodine Emission from KI_x Impregnated Carbons

The retention of iodine by KI_x carbons in service is a very desirable property. Should elemental iodine be retained by physical adsorption, it would be readily desorbed after only a small temperature increase. Iodine, however, held by chemical combination with the carbon network, would require a higher temperature to decompose the carbon iodine covalent bond (23). A chemical modification of the carbon network and of iodine-containing impregnants by weathering can also adversely influence the retention since the surface composition is modified by the contaminants.

Thermal analyses of new, and service-weathered KI_x carbons were made in order to observe possible changes in iodine bonding to the base carbon. Laboratory tests were conducted by a controlled temperature increase of the carbon and the measurement of the release of iodine to the air flow in addition to the gasification of carbon (CO and CO₂). The temperature gradient was 3°C/min and the upward air flow through the carbon bed (2.54 cm diameter and 2.54 cm depth) was 5 L/min. The effluent elemental iodine from the heated carbon sample was determined as evolved, and in an independent determination, the effluent iodine was converted completely to elemental by passage of the aliquot through a hot quartz tube before the iodine measurement (24). Both new test carbon (MSA) and carbons obtained from the Three Mile Island Nuclear Power Station (see Table 31) were subjected to thermal analyses.

Table 31. Samples Subjected to Thermal Analysis for Iodine and Oxides of Carbon

Test No.	Sample	Source
3342	2652	A train, Aux. Bldg., Unit 2
3343	2603	B train, Fuel Handling, Unit 2
3344	2525	B train, Aux. Bldg., Unit 2
3345	2759	A train, Fuel Handling, Unit 2
3351	-	New MSA, 463563

The rates of elemental iodine (mg/M^3) thermal emission from the above service carbons are given in Figs. 20 to 23 as a function of the exit gas temperature. In each case, a comparison was made with a sample of new MSA 463563 carbon. The emission from each service carbon exceeded that from the new MSA carbon; also, the rate increased more rapidly in the lower temperature range for the service carbon. It is concluded that the iodine in a KI_x impregnation of the carbons is subject to chemical change as a result of the weathering process.

The above service carbons were aligned in Table 32 in sequence of decreasing penetration of methyl iodine-131 in order to determine whether the degradation processes to which these KI_x -impregnated carbons were subjected might be correlated with weathering. Did the iodine emission increase in the same sequence as the observed methyl iodide-131 penetration? The total iodine (mg) gasified at 180° , 221° , and at the spontaneous ignition temperature (SIT) are given in Table 32. The sequence is shown to have the same alignment at the SIT as do the corresponding determinations of methyl iodide-131 penetration. The only anomaly is the A train (2759) of the Fuel Handling Building, but the available data do not allow a detailed mechanism to be determined.

Table 32. Comparison of 131-ICH_3 Penetration with Iodine Emission

Carbon	CH_3 I-131 Penetration	Total Iodine Emission, mg		
		180°C	211°C	SIT
2603	50.9	2.71	4.50	18.5
2525	44.0	2.03	3.56	-
2652	30.5	0.63	2.0	14.0
2759	24.5	1.60	3.07	13.9
New MSA 463563	0.13	0.24	0.82	9.7

The two independent phenomena appear to be interrelated. The various stages of weathering should be re-examined for a possible correlation between CH_3 I-131 trapping and the thermal stability of the iodine impregnation (KI_x).

The rate of iodine emission with increase of temperature reached an approximately steady rate between 200 and 250°C (see Figs. 20-23.) The rate then decreased somewhat to the same level as, or somewhat lower than, the new MSA material. A determination was made of the iodine impregnated in each carbon and the fractional loss of iodine during the oxidation up to the SIT was estimated. The results (Table 33) indicate that the iodine emission indeed increased as a consequence of weathering or service. Since at most only 6% of the total iodine was emitted at the SIT, the leveling-off of the rate near the SIT is not a result of exhausting the iodine in the impregnated carbon. Above the SIT, the iodine was rapidly evolved, but the rate could not be determined because of saturation of the iodine detector.

Table 33. Thermal Emission of the Iodine Impregnated in the Carbon

Carbon	Sample wt (g)	Wt.% I	Impregnated Iodine (mg)	Total Iodine Emitted (mg)	
				at SIT	%
2603	6.39	4.8	306	18.5	6.0
2525	6.37	2.3	147	-	-
2652	5.76	5.8	334	14.0	4.2
2759	5.74	5.0	287	13.9	4.8
MSA 463563	6.57	4.2	276	9.7	3.5

Organic iodine compounds were present in the evolved fraction during the early stages of the heating cycle, but the amounts were small relative to elemental iodine. This observation agrees with previous results with a KI_x -impregnated carbon (2701) which did not form significant amounts of organic iodides as gas phase products in an oxidation (13).

In all of the samples analyzed, the iodine released was accompanied by carbon oxidation to form CO and CO₂. The amount of carbon burn-off (i.e., that contained in the CO + CO₂) was qualitatively proportional to the elemental iodine evolved. The behavior has been explored in some detail since it would suggest the rupture of a strong bond between impregnated iodine and the carbon networks of a KI_x impregnated carbon. The lower

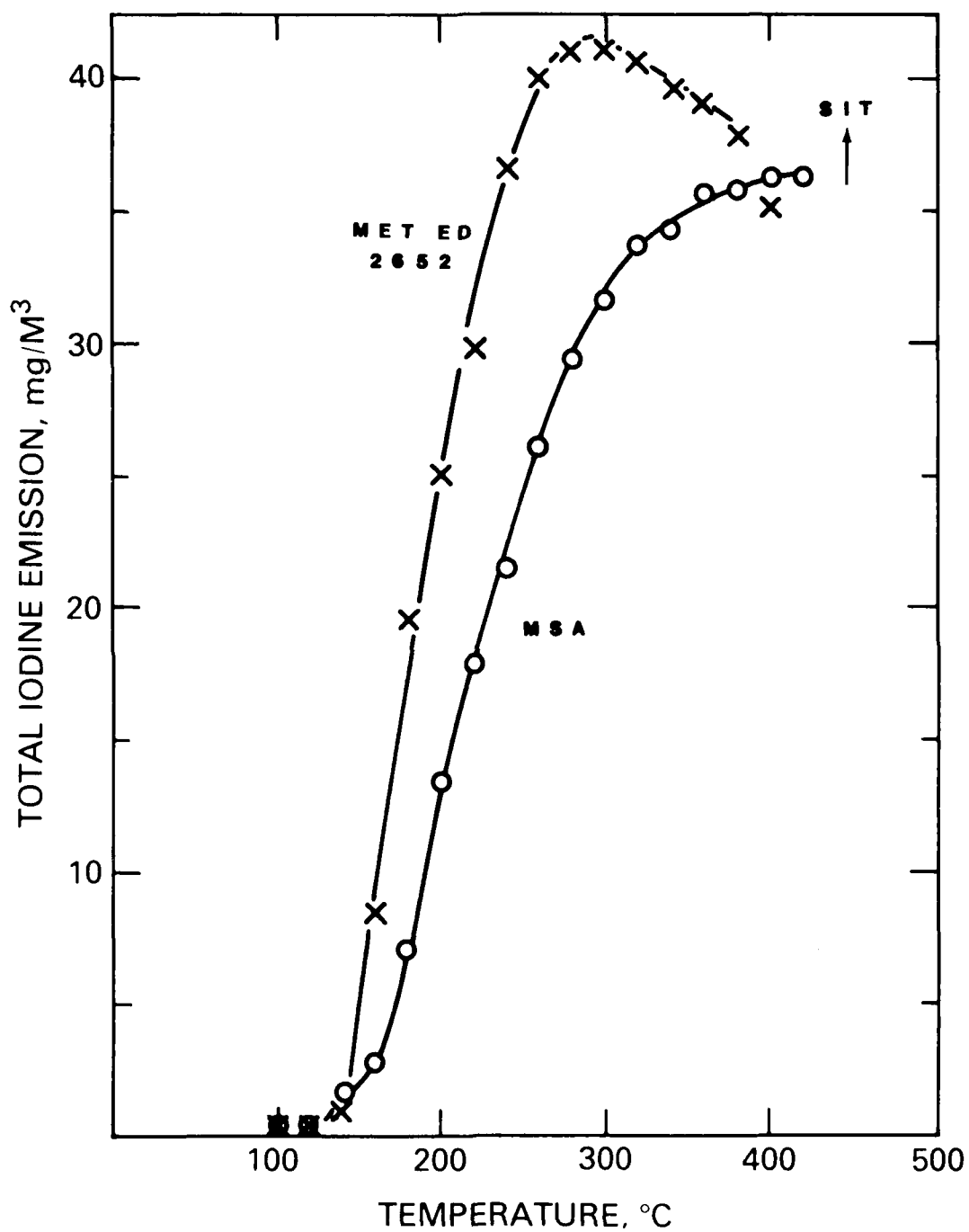


Figure 20. Rate of Iodine (I_2) Emission with Temperature Programmed at $30^\circ/\text{min}$ for MET ED 2652 (NRL Test 3342)

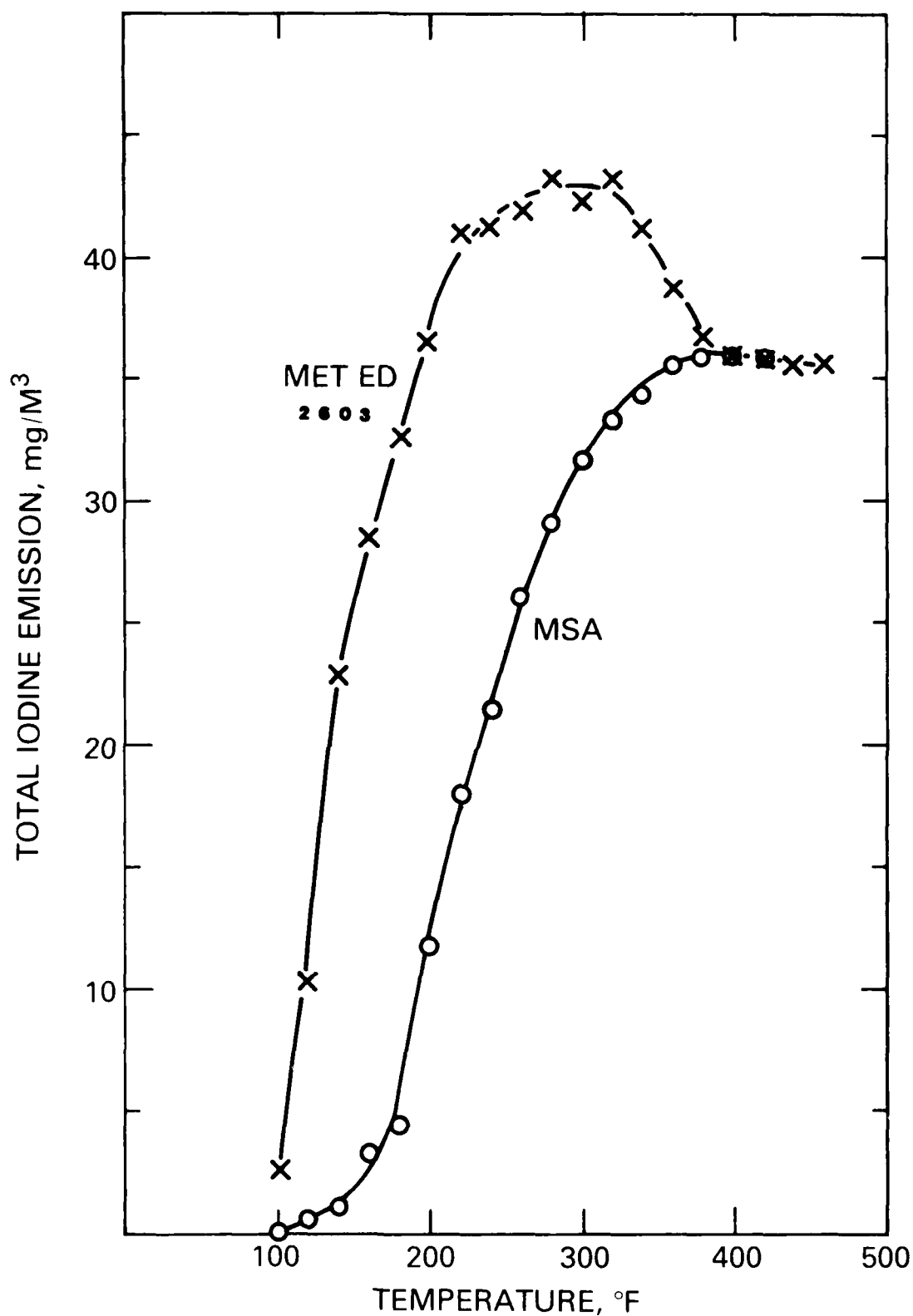


Figure 21. Rate of Iodine (I_2) Emission with Temperature Programmed at $30^\circ/\text{min}$ for MET ED 2603 (NRL Test 3343)

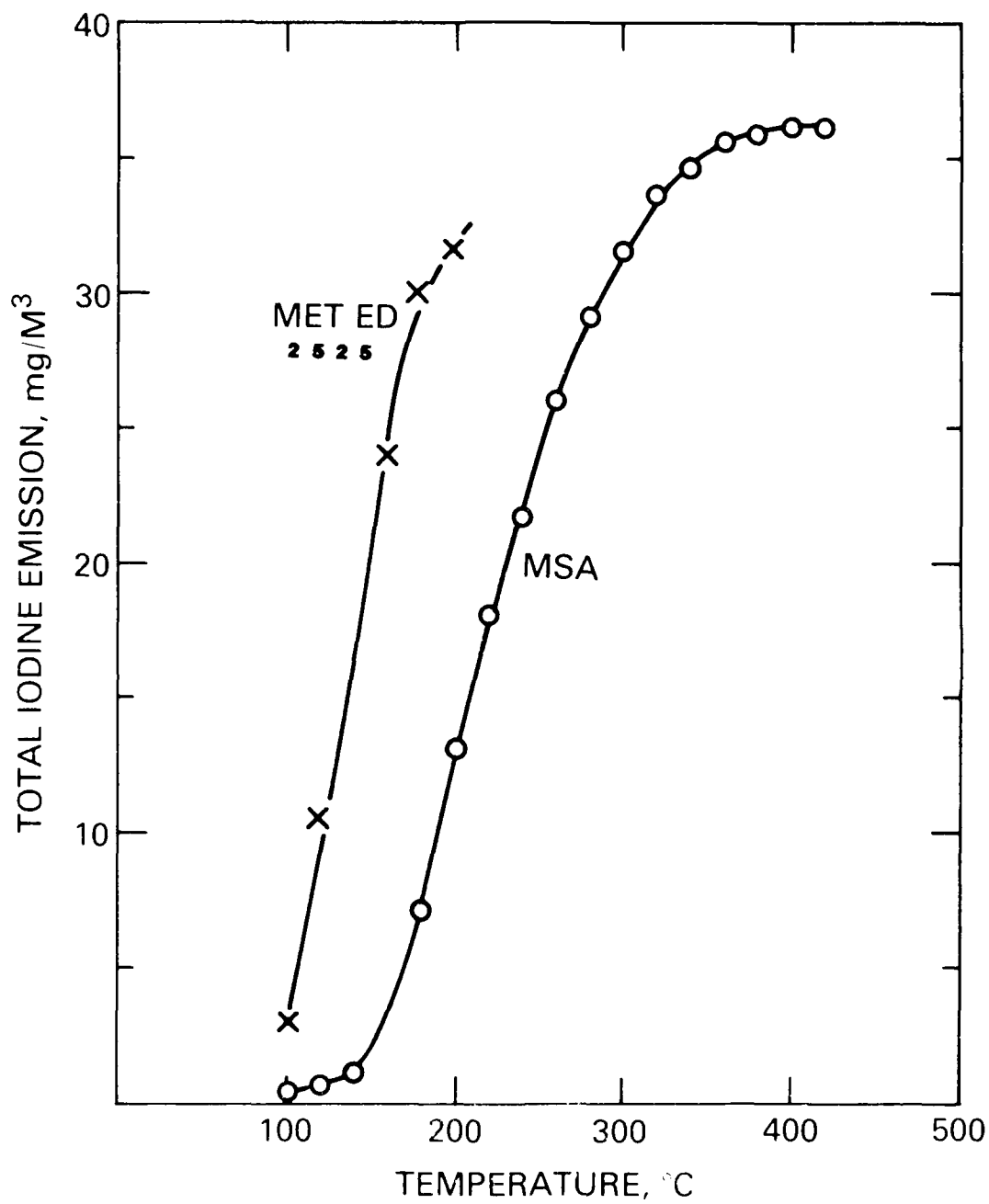


Figure 22. Rate of Iodine (I_2) Emission with Temperature Programmed at $3^\circ/\text{min}$ for MET ED 2525 (NRL Test 3344)

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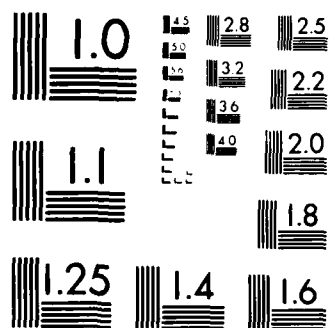
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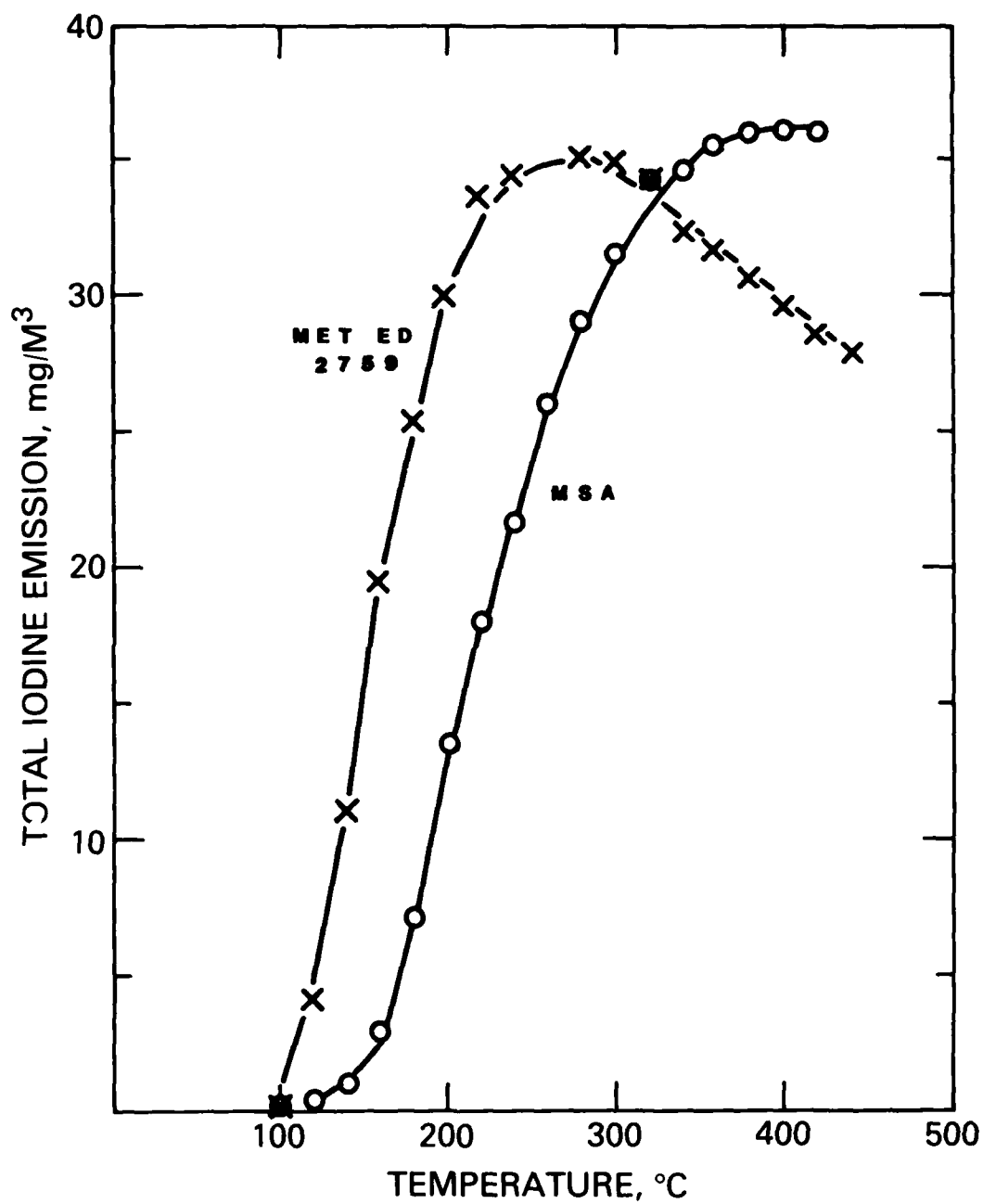


Figure 23. Rate of Iodine (I_2) Emission with Temperature Programmed at $3^\circ/\text{min}$ for MET ED 2759 (NRL Test 3345)

section of Fig. 24 compares the total iodine released from the various carbons as a function of the total carbon burn-off (CO and CO_2) up to 180°C using the four carbons of Table 31. The same is shown in the upper section of Fig. 24 when integrated up to 360°C . There is a correlation trend in both cases.

The total carbon gasified using the MET ED 2603 sample is plotted in Fig. 25 as a function of the elemental iodine released. The X-coordinate is turned back after 3 decades and then continued in the upper section to cover three additional decades.

The ratio for the above measurements of carbon gasified to iodine released expressed in stoichiometric quantities, is plotted in Fig. 26. The ratio was found first to decrease as the temperature increased to about 160° , and then to increase at higher temperatures. The behavior in both Fig. 25 and 26 is compatible with a model in which there is a threefold increase of I_2 up to 160°C and less than a one-fold increase in total carbon; this could be termed desorbed or easily decomposed iodine. In the temperature range $160\text{--}400^\circ\text{C}$, there is an additional threefold increase of I_2 and about a threefold increase in gasified carbon; this behavior indicates decomposition of a stronger iodine-carbon bond. The dotted line in the upper section of Fig. 25 indicates a 1 to 1 mole ratio of carbon to iodine. In all cases, the weathering of a carbon realized during service results in an enhancement in the release of impregnated iodine.

The two new KI_x carbons, MSA and BC 727, have the same general behavior in carbon burn-off and iodine release (shown in Fig. 27), but they differ in degree. For a given level of carbon (from $\text{CO} + \text{CO}_2$), less total I_2 is released over the five decades from the BC 727 sample than from the MSA sample. Alternatively, to realize a given iodine release, more carbon had to be gasified from BC 727 than MSA. The increase of I_2 (two decades) from 26 to 50°C with relatively little carbon burn-off is compatible with physical desorption of I_2 , but at the higher temperatures, there is steady carbon burn-off along with iodine release.

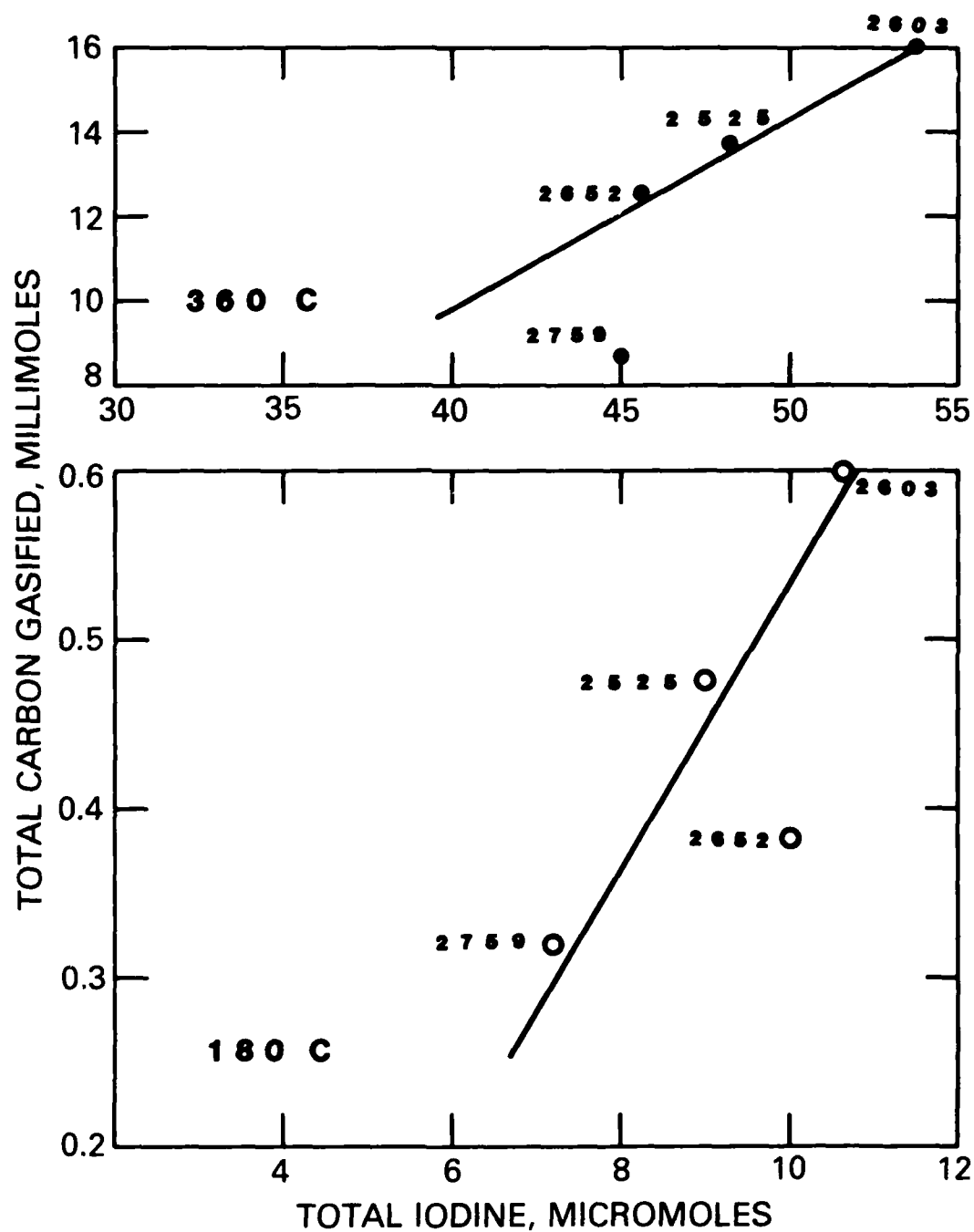


Figure 24. Correlation Using Four TMI Carbons Between the Total Carbon Gasified and the Total Iodine Released Integrated to 180°C (Bottom) and to 360°C (Top)

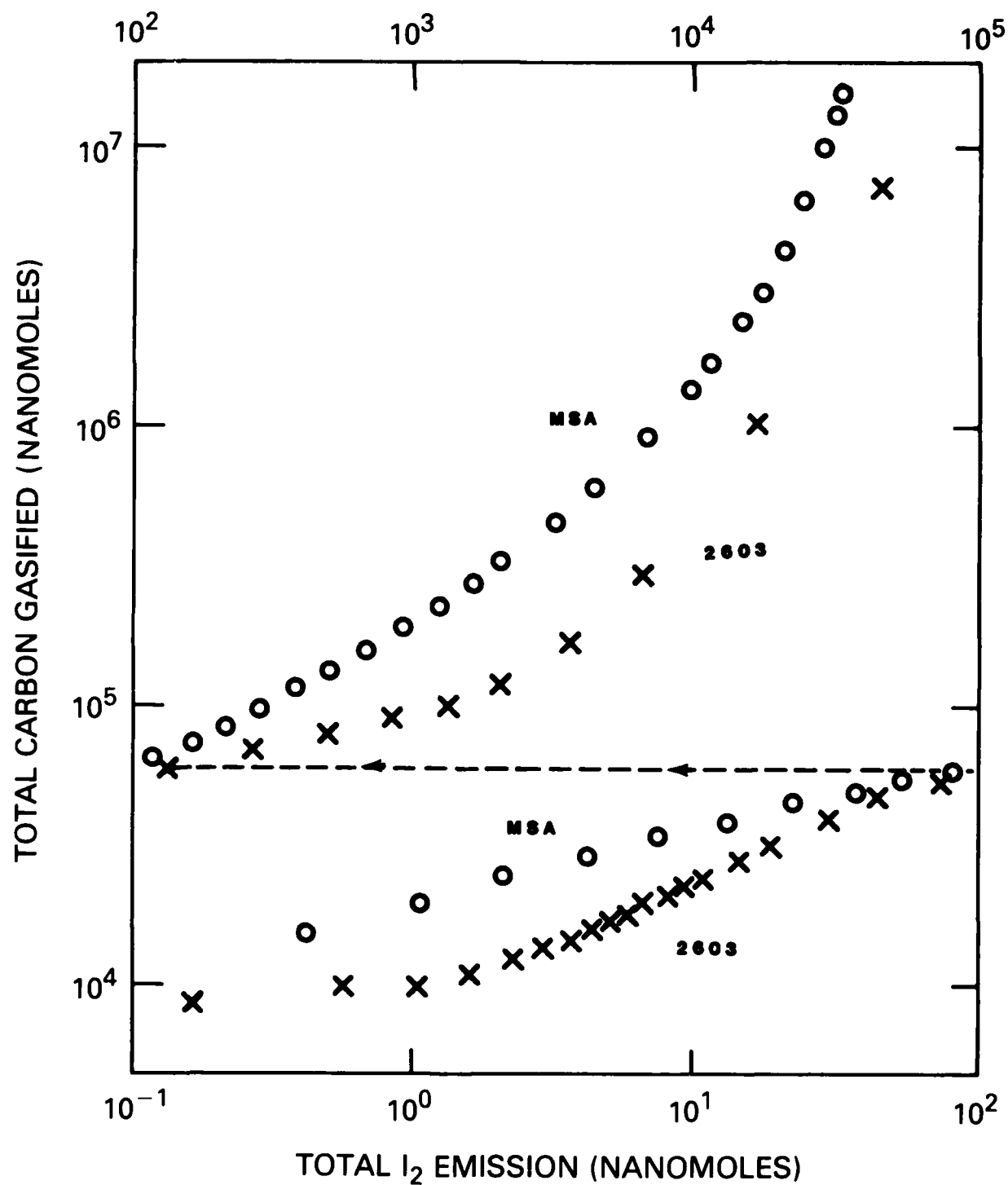


Figure 25. Correlation of Carbon Gasified with the Release of I_2 for MET ED 2603

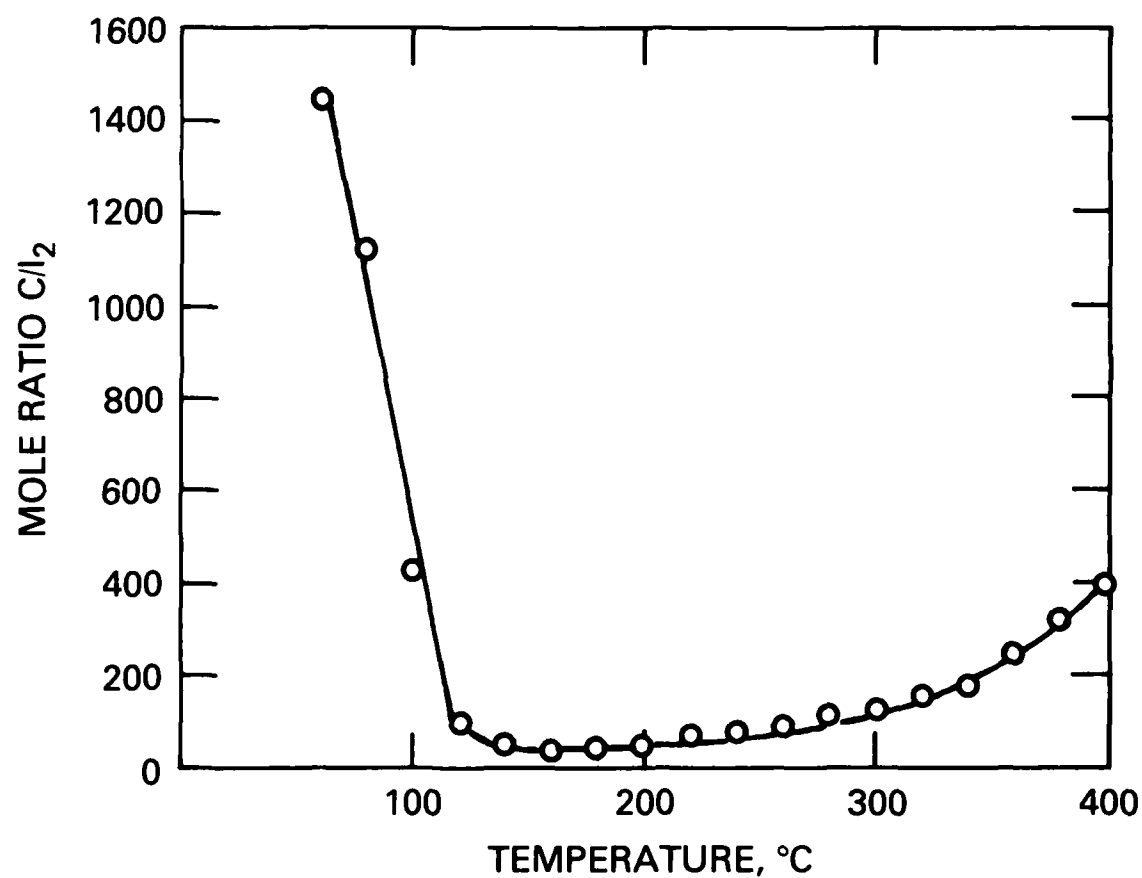


Figure 26. Mole Ratio of the Carbon Gasified to the Iodine Released as a Function of Temperature for MET ED 2603 (NRL 5154)

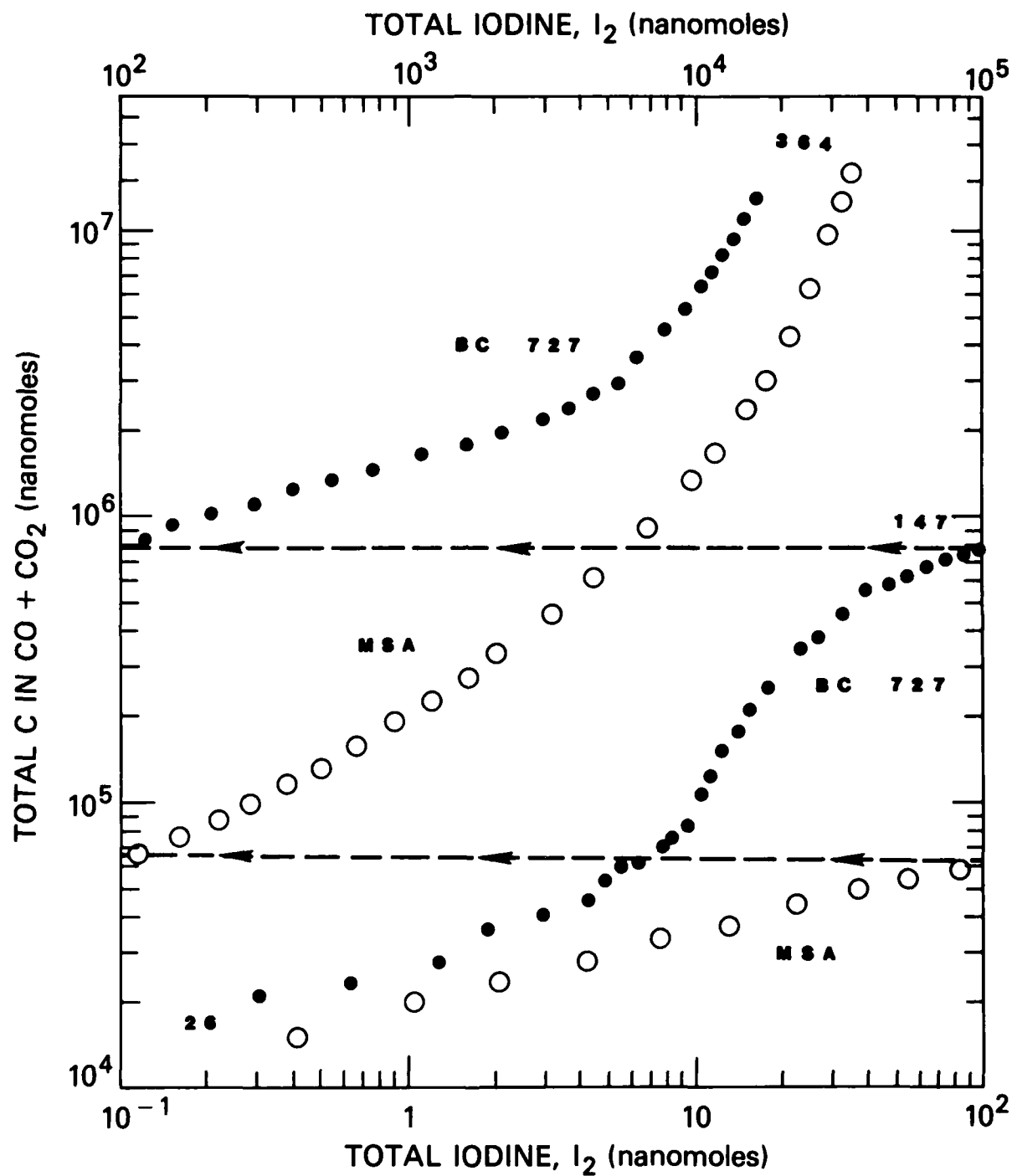
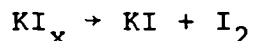


Figure 27. Correlation of Carbon Gasified with the Release of I_2 for Two New KI_x Carbons, BC 727 and MSA
463563

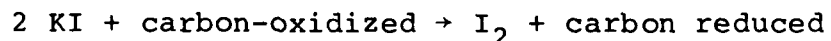
The above measurements may be summarized as follows:

1. The weathering of a KI_x carbon modifies the thermal stability of the impregnated iodine and causes a greater emission of elemental iodine at lower initial temperatures.
2. The carbon is gasified to CO and CO_2 and the increase is proportional to the iodine evolved.
3. The magnitudes of the CH_3I -131 penetration of corresponding samples are in the same sequence as the total iodine emissions when the latter are compared at the same temperature.
4. The total iodine released, integrated up to the SIT, is considerably less than that contained in the impregnation formulation.

The dominant iodine species in the thermal emission from KI_x carbons is the I_2 molecule which can result from several reactions. If the KI_x species is present on the carbon as a molecular entity, a simple decomposition would take place:



If the iodine in KI is oxidized, another species on the carbon must be reduced. The process may be formulated as follows:



A sink for the K^+ in KI is most likely the carbonate or bi-carbonate. However, it is more likely that the actual mechanism is quite complex due to the great heterogeneity of the carbon surface composition. The heat of dissociation of the carbon-iodine bond varies with the molecular species; the value for CH_3I is 50 kcal/mole. The decomposition of all iodine species on a weathered KI_x impregnated carbon would lead to a continuous emission of iodine.

5.2 Formation of Organic Iodine Compounds

The direct formation of organic iodides by the reaction of elemental iodine and an activated carbon is an important fact to establish. It is necessary to use a base carbon alone in order to remove the contribution of the impregnation chemicals.

A mixture of elemental iodine (0.5 wt.%) and an activated carbon (BC Type 177) from coconut shells was heated ($6.7^{\circ}\text{C}/\text{min}$) in a flow of purified air at a linear velocity of $10\text{m}/\text{min}$. The effluent gas was first directed into a micro-coulometric detector, the calibration of which has been reported (24). A second experiment was then conducted in which the effluent gas passed through a heated quartz pyrolyzer tube which had been shown to decompose organic iodides quantitatively.

The results, shown in Fig. 28 and Fig. 29 indicate that some elementary iodine was detected almost immediately and organic iodide was detected as low as $100\text{--}125^{\circ}\text{C}$. Two other activated carbons - BPL 10X16, a coal base carbon, and GX 32, a petroleum base carbon - were also studied. A comparison was made (Table 34) of the products integrated to 180°C and to 260°C . The coconut carbon at 180°C released only 0.00055 wt.% elemental iodine, the coal base carbon released about four times more, 0.0023 wt.%, and the petroleum carbon base material released ten times more. However, the formation of organic iodides is in the reverse order, in that the coconut carbon emitted ten times more organic than elemental carbon, the coal base carbon emitted only 30% more, and the petroleum base less than 10% more. When the release was integrated to 260°C , the pattern was about the same.

Mixtures of the carbons with either methyleneiodide (CH_2I_2) or iodoform (CHI_3) also released both elemental iodine and organic iodides upon heating in the same temperature range. It is apparent that a mixture of I_2 and organic compounds will form in the heating of an activated carbon with any starting mixture that contains iodine.

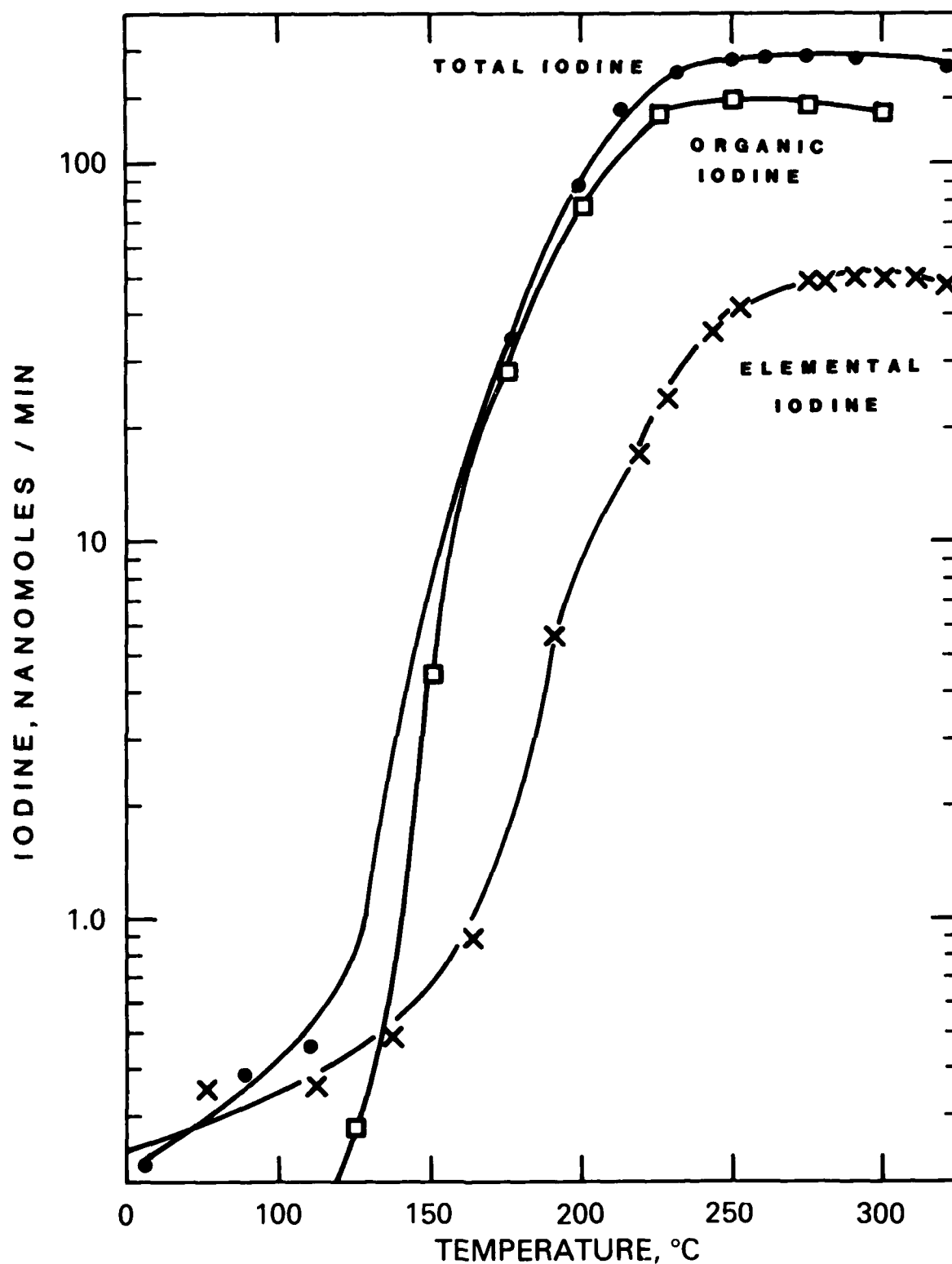


Figure 28. Formation of Organic Iodides from a Mixture of Elemental Iodine and Non-impregnated Coconut Activated Carbon (Note: y coordinate is logarithmic)

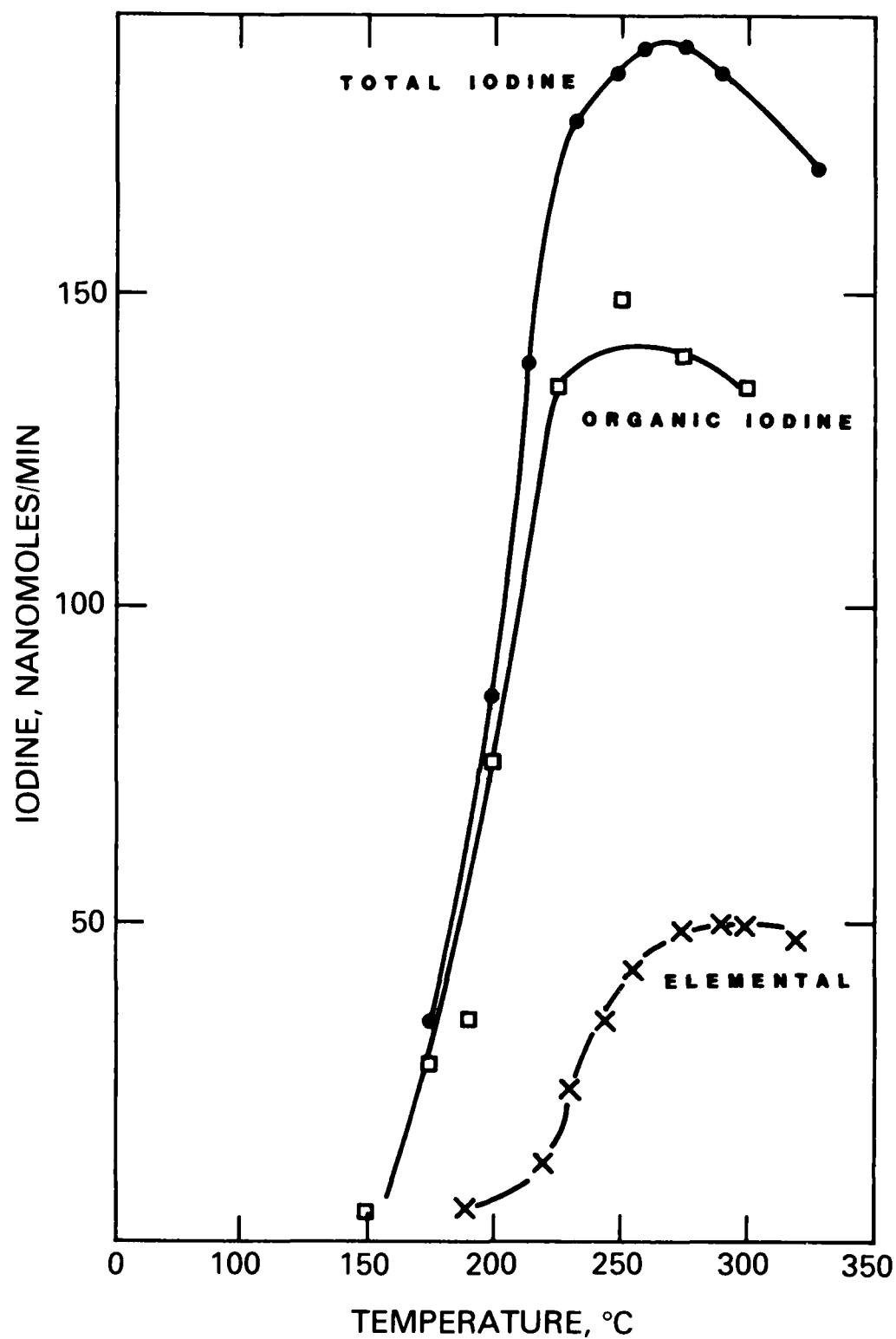


Figure 29. Formation of Organic Iodides from a Mixture of Elemental Iodine and Non-impregnated Coconut Activated Carbon (Note: y coordinate is arithmetic)

Table 34. Thermal Release of Iodine from Mixtures of I₂ and Base Carbons

Carbon	Detection Systems	Initial I ₂ (mg)	Integrated to 180°C		Integrated to 260°C	
			(mg)	Wt. %	(mg)	Wt. %
BC 177	I ₂	25.6	.00014	.00055	.0043	0.017
BC 177	I ₂ + Organic	25.6	.00194	.0076	.0269	0.11
BPL 10x16	I ₂	29.5	.000682	.0023	.0316	0.11
BPL 10x16	I ₂ + Organic	29.5	.000891	.0030	.0366	0.12
GX 32	I ₂	17.1	.00408	.024	.0090	0.35
GX 32	I ₂ + Organic	17.1	.00442	.026	.0094	0.41

VI. Discussion

6.1 Dependence of $^{131}\text{ICH}_3$ Trapping Efficiency on Water Vapor

It has been well established by many independent studies that the trapping efficiency of nuclear-grade carbons for $^{131}\text{ICH}_3$ is adversely influenced in air flows of high relative humidities (10,11,12). The results in Table 27, Section 4.6, show that the weight gains of the carbons due to 100 hr. exposures in air flows at designated relative humidities increase more for KI_x impregnations than for those containing TEDA. The latter behavior is given by the dotted curves in Fig. 30; G 615 contains both KI_x and TEDA impregnations, and S&S contains only TEDA.

The penetrations of $^{131}\text{ICH}_3$ in air flows of different relative humidity for the above carbons, Fig. 18, can be divided in the same grouping. The S&S carbon had least penetration at 90% RH, with G 615 next. The KI_x -impregnated carbons showed greater penetration, however, not quite in the same order of weight percent increase.

Table 35. The Penetration of Methyl Iodide-131 through the Conditions of the Exposure

NRL Test	Time (Mos)	Termination Date	Dew Points °F			Penetration %
			S-2	S-1	S	
5022	3	30 Sep 77	52°	45°	51°	1.84
5097	3	1 Sep 78	71	72	69	3.13 ± .03
5099	3	1 Sep 78	71	72	69	3.10 ± .049
5058	6	1 May 78	35	38	19	0.61 ± .17
5057	9	16 Aug 78	75	77	77	6.62 ± .20

The two samples (5097, 5099) exposed to outdoor air at NRL during the same three-month period ending 1 September 1978, gave the reproducibility indicated in Table 35 for the penetration values. Included are the uncertainties of sampling, those inherent in weathering and those in the determination of the penetration. The mean value for penetration of 3.12 is based on too few measurements for statistical analysis. The test 5022, also for three months ending 30 September 1977, showed less

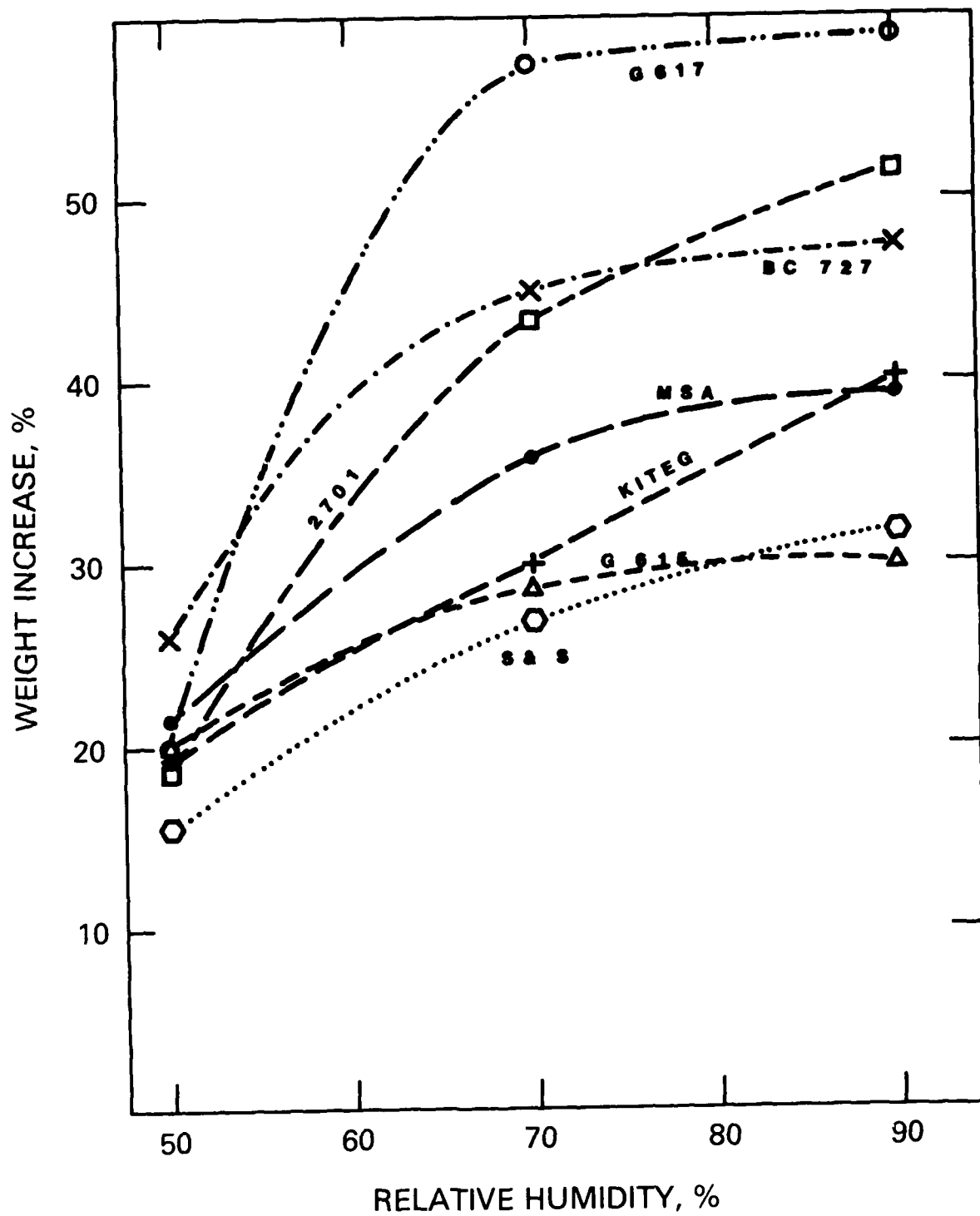


Figure 30. Weight Gains (%) of Carbons After 100 hr Exposures to Air Flows at Designated Relative Humidity.

penetration, but this behavior may be correlated with the lower dew point just before sampling. In Table 35, Column S-2 gives the dew points two days before termination of the exposure, S-1 gives values one day before, and Column S corresponds to the day of termination. Sample 5058 weathered for six months, terminated on 1 May 1978 during a period of rather dry weather (very low dew point), and showed only 0.61% penetration. After nine months of weathering, the sample of G 615 showed a high penetration (6.62% in Mode 2) and a corresponding low acidity of the entrance layer (pH = 4.1).

The above results are yet another example of the effect of water adsorption on nuclear carbons and the subsequent penetration of $^{131}\text{ICH}_3$. The separate contributions of adsorbed contaminants and water vapor and the synergistic influence during the weathering of test carbons are critical factors that determine the efficiency during service. The reduction in the partial pressure of water during the period of low-humidity weather may function as a regeneration process with respect to a partial recovery of the $^{131}\text{ICH}_3$ trapping efficiency.

The weight gain of a nuclear carbon was found to respond to the meteorological conditions during the exposure. For example, NCAR 617 was exposed for one month in June 1977 and in July 1977. The data for the two tests with the nuclear carbon are summarized in Table 36. The moisture content of the air was less in June than in July and accounts for the twofold increase in adsorbed moisture of the July sample. By reference to Fig. 19, however, it is seen that the increase comes in the critical region where the penetration increases sharply with relative humidity. As a result, a seven- to eight-fold increase in penetration was realized.

The attempts to correlate the one-month exposures of BC 727 with meteorological data are summarized in Fig. 31. The monthly average dew point and temperature for each exposure are given in Table 37 with the observed penetration of $^{131}\text{ICH}_3$. The latter is plotted (Fig. 31) as a function of dew point, relative humidity, or the quantity of water vapor that were present

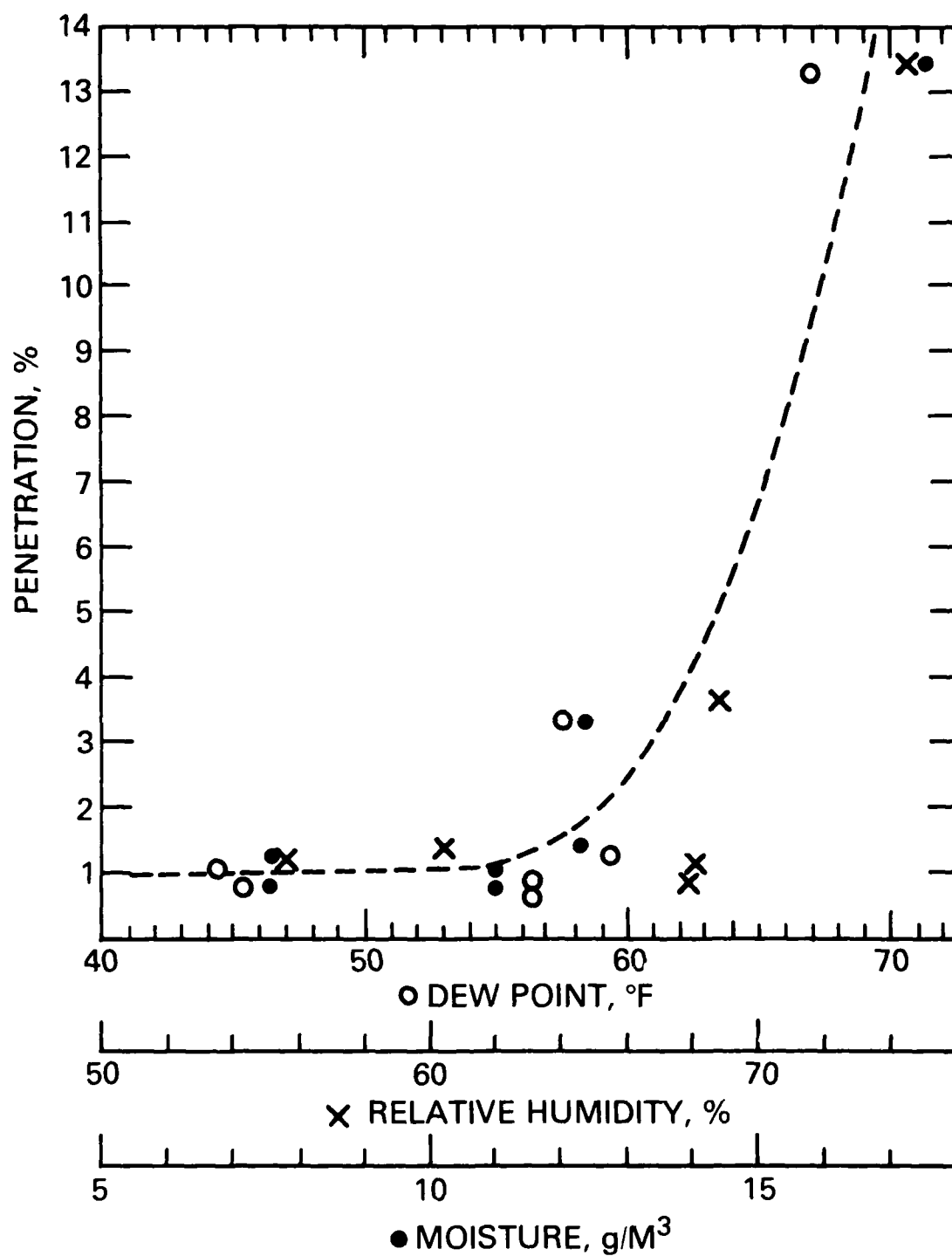


Figure 31. Penetration of $^{131}\text{ICH}_3$ Through BC 727 After One-Month Exposure to Outdoor Air

Table 36. Performance After One-Month Exposures of NACAR 617
(June and July 1977)

	June	July
Average Temperature (°F)	74°	80.9°
Average Dew Point (°F)	59°	67°
Weight Increase - Layer 1	22.2%	45.9%
2	20.3	46.3
3	18.8	44.9
4	16.9	42.6
Penetration - Layer 1	1.9%	12.9%
2	0.62	-
3	0.32	-
4	0.64	5.4

during exposure. The penetration increased sharply within the same range since these parameters are interrelated. The behavior is similar to that previously reported for laboratory exposures with water vapor-air flows.

Table 37. Performance After One-Month Exposures of BC 727

Sample	Date	Avg. Temp. °F	Avg. Dew Point	Penetra- tion %
5014	2-30 Jun 77	74	59	1.30
5070	7 Jan - 2 May 78	60	44	1.13
5081	2 May - 2 Jul 78	69	56	0.92
5082	2 May - 2 Jul 78	69	56	0.69
5083	2 May - 2 Jul 78	69	56	0.83
5113	2 Aug - 1 Sep 78	79	68	13.2
5124	13 Oct - 14 Nov 78	58	45	0.81
5121	1 Sep - 13 Oct 78	70	57	3.31

Frequently, a carbon filter in a nuclear power installation is placed on a standby basis and thus is used with intermittent air flows. One result of such operations may be to redistribute the adsorbed contaminants through surface mobility over the large area of the activated carbon. Adsorbed molecules are known to diffuse in directions parallel to the surface and the extent varies with the potential energy barrier that exists. Low boiling hydrocarbons, for example, may diffuse with less restraint than a strongly held contaminant like ozone.

In order to observe the possible influence of "resting" impregnated activated carbons, three samples (BC 727, NACAR G 615, and Sutcliffe and Speakman 5% TEDA) were exposed for known periods of outdoor air flow and standby. The weathering was conducted for one month, then held inactive by a secure closure of the inlet and outlet, and then again exposed for an additional month. An additional off-on cycle was added in two cases. The schedule of these exposures is summarized in Table 38, where n is the number of filter displacements and t is the average residence time during the exposure periods.

Table 38. Schedule for Intermittent Weathering in Exposure to Unmodified Outdoor Air at NEL

Test	Carbon	Time (Hours)	Volume (10 ⁶ cu ft)	Exposure Dates 1978	Total Exposure (Months)	n _g (10 ⁶)	t (sec)	Pene.
5074	BC 727	On 1077	.1704	2 Jun - 17 Jul	2.5	11.7	.33	(11.8+.302)%
		Off 768	-	17 Jul - 18 Aug		7.94	.34	
		On 744	.1155	18 Aug - 18 Sep				
	Total	On 1821	.2859					
5095	BC 727	On 1077	.1677	2 Jun - 17 Jul	3.7	11.6	.34	(12.0+.106)%
		Off 768	-	17 Jul - 8 Aug		8.18	.33	
		On 745	.1186	18 Aug - 10 Sep				
		Off 720	-	18 Sep - 18 Oct		9.97	.32	
		On 888	.1450	18 Oct - 24 Nov				
	Total	On 2710	.4313					
5112	S&S	On 740	.1150	18 Jul - 18 Aug	3.0	7.91	.34	(.019+.002)%
		Off 744	-	18 Aug - 18 Sep		7.99	.32	
		On 720	.1162	18 Sep - 18 Oct				
		Off 720	-	18 Oct - 18 Nov		6.77	.35	
		On 672	.0985	18 Nov - 18 Dec				
	Total	On 2132	.3297					
5111	G 615	On 740	.1156	18 Jul - 18 Aug	2.0	7.95	.34	(.089+.014)%
		Off 744	-	18 Aug - 18 Sep		8.01	.32	
		On 720	.1165	18 Sep - 18 Oct				
	Total	On 1460	.2321					

Although more of these measurements should be undertaken, the intermittent weathering of BC 727 appears to be more degrading than continuous operations with the same carbon. A summary of the results for BC 727 is given in Table 39.

Table 39. Intermittent Exposures of BC 727 to Outdoor Air

Test	Operation	Total Exposure Time (Mos.)	Penetration %
5032	Continuous	2	3.56
5065	Continuous	2	6.84 \pm .12
5096	Continuous	2	3.79 \pm .16
5020	Continuous	3	7.59
5094	Intermittent	2.5	11.8 \pm .302
5095	Intermittent	3.7	12.0 \pm .106

Corresponding results for another nuclear carbon, NACAR G 615, which contained TEDA as part of the impregnation, indicate a different behavior (Table 40).

Table 40. Intermittent Exposures with NACAR G 615

Test	Operation	Time (Mos.)	Penetration %
5031	Continuous	2	1.41
5022	Continuous	3	1.84
5111	Intermittent	2	0.09

The "resting" of the filter in this case appeared to reduce the subsequent penetration of $^{131}\text{ICH}_3$. The difference in behavior may be due to the type of impregnation. The G 615 contains, among other things, some TEDA, and the BC 727 contains KI_x in the impregnation. The TEDA of the impregnation appears to be stable in the environment of the adsorbed contaminants and, in fact, improves during "resting". Additional larger-scale studies are needed to include the influence of the changing concentrations of moisture that existed during the exposures to outside air and in the period just before the termination of the weathering.

Future investigations may benefit from the good control available in laboratory exposures rather than with outside air.

Ackley, Adams and Browning (10) recommended that in the design of a $^{131}\text{I}\text{CH}_3$ removal system, that some provision be provided to maintain the prevailing relative humidity below 90% RH. A simple procedure to accomplish this would be to pre-warm the air flow to the carbon. To reduce 95% RH air at 77°F to 50% RH requires a temperature increase of 18°F, and to reduce 95% RH air to 70% RH requires 9°F (see Fig. 32). The disadvantage is, of course, the heating costs of the large volume of air in process. Heating estimates to reduce the relative humidity of inlet air for time periods at designated relative humidities and to reach target values of 70 to 50% RH are summarized in Table 41. Since the inlet air is not always at 95% RH, some consideration should be given to the use of controlled inlet air heaters on ventilating systems based on a technical and economic analysis of the engineering factors.

Table 41. Heating Estimate to Reduce the Relative Humidity of Inlet Air to Either 50 or 70% RH for a Carbon Unit of 30,000 cfm

Fraction of Inlet Air at Designated Relative Humidity			Required Heat (BTU) to Reach Designated Target	
95% RH	70% RH	50% RH	50% RH	70% RH
1.0	0	0	3.96×10^9	1.98×10^9
.5	.5	0	2.97×10^9	0.99×10^9
.25	.5	.25	1.98×10^9	0.50×10^9
.20	.4	.40	1.58×10^9	0.40×10^9
.10	.40	.50	1.18×10^9	0.20×10^9

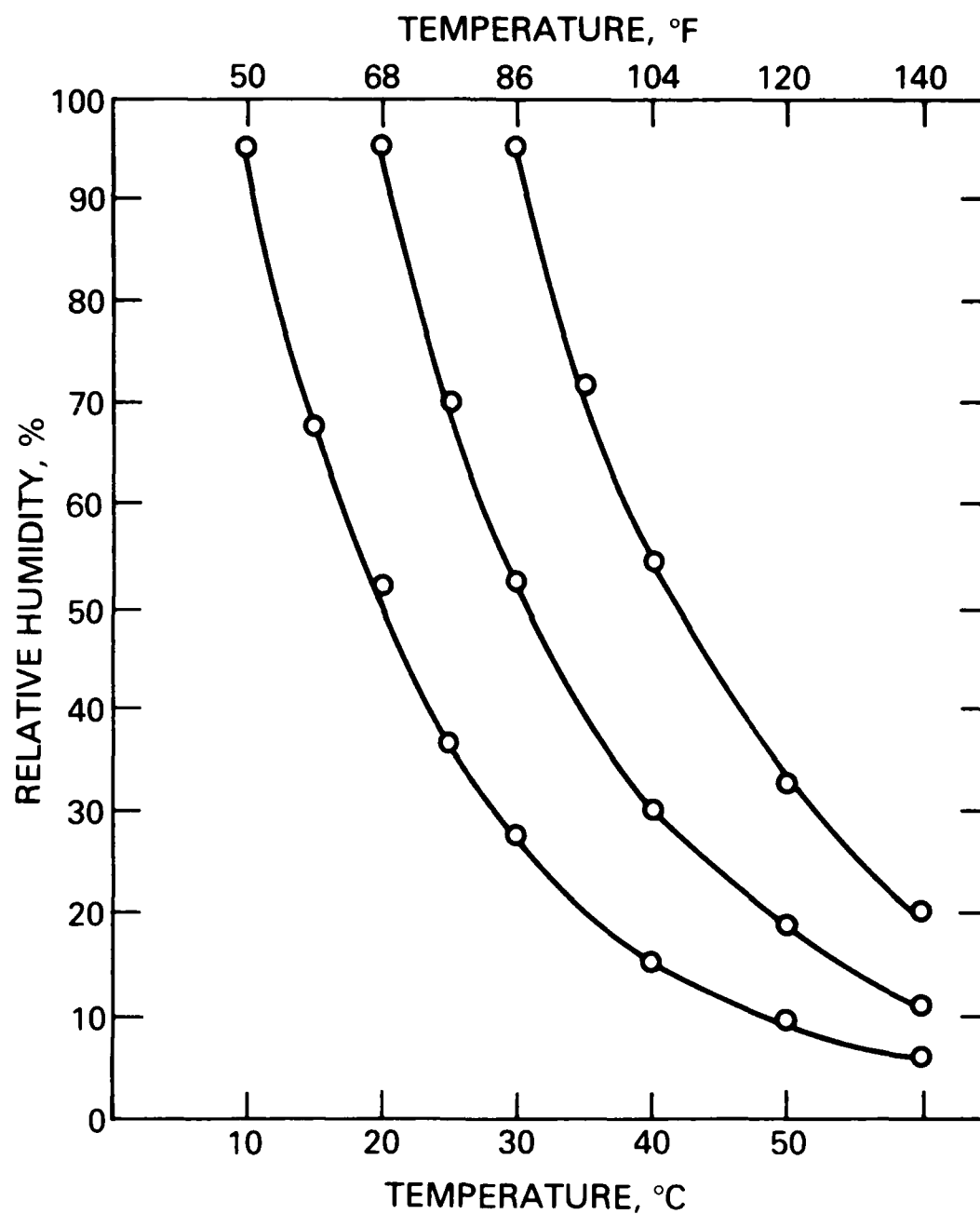


Figure 32. Decrease in Relative Humidity on Heating Air Initially at 95% RH at the Designated Temperature

6.2 Depth Profile in Weathered Nuclear Carbons

As a function of exposure time, the depth profile through a carbon bed has demonstrated that the top layer serves as a guard layer for the remaining carbon. The pH of the water extract of the first half-inch layer of the two-inch bed becomes progressively acidic with time of exposure. The results in Table 42 show that the pH may drop below 3.0 after a year's exposure at the NRL site (see also (17)).

Table 42. Values of pH of the First Half-Inch Layer of a Two-Inch Bed After Exposures at NRL

Exposure (months)	G 615	BC 727	2701	KITEG	S & S	MSA 463563
1	9.3	8.3	7.6	6.7	8.0	7.5
2	8.2	7.6				
3	7.9	7.0	3.6	2.8	4.5	3.4
6	3.8	3.1	2.4	2.4	4.0	2.5
9	4.1	3.3	2.5	2.3	3.2	2.7
12	2.9	2.2				

The behavior of two of these carbons at two other weathering sites has been followed for a shorter time, but, as shown in Table 43, the trend towards lower pH with exposure time is present.

Table 43. Values of pH of the First Half-Inch Layer of a Two-Inch Bed

Time (mos.)	<u>Argonne Site</u>		<u>Simi Valley</u>	
	BC 727	G 615	BC 727	G 615
Original	9.5	9.8	9.5	9.8
1.3	7.9	8.8	-	-
4	6.4	7.0	6.9	8.0
7	6.8	6.8	6.5	8.5

(continued)

Table 43 (continued)

Time (mos)	Argonne Site	Simi Valley
	S & S	S & S
Original	9.5	9.5
2.5	6.8	6.4
5	4.5	3.8

The weight increase in the first half-inch layer of the test carbon has no trend with exposure time since most of the weight change depends strongly on the moisture content of the air at the point in time of sample withdrawal. The behavior for six of the carbons under study is shown in Table 44.

Table 44. Weight Increase of the First Layer of a Two-Inch Bed at NRL Exposure

	G 615	BC 727	2701	KITEG	S & S	MSA 463563
1	21.7	3-46*	27.1	16.8	0 to 25.7	20-30
2	21.3	36.2**				
3	34	34.5	5.5	9.2	5.9	5.0
6	6.5	9.1	27.0	27.0	30.7	8.0
9	36.4	47.4	45.5	29.6	26.5	9.2
12	23.6	28.9				

* Range of many determinations
 ** Averaged

All new carbons show a simple exponential attenuation of $^{131}\text{ICH}_3$ penetration with depth (see Figure 6, page 18). In weathered or service-aged carbons, the depth profile is quite unpredictable. As shown in Figs. 33 and 34, the greatest penetration is through the inlet layer of the carbon and the penetration through each of the remaining beds tends to a constant value, but the penetration is considerably more than the original new carbon. This behavior is compatible with some uniformity in the degradation below the inlet carbon layer.

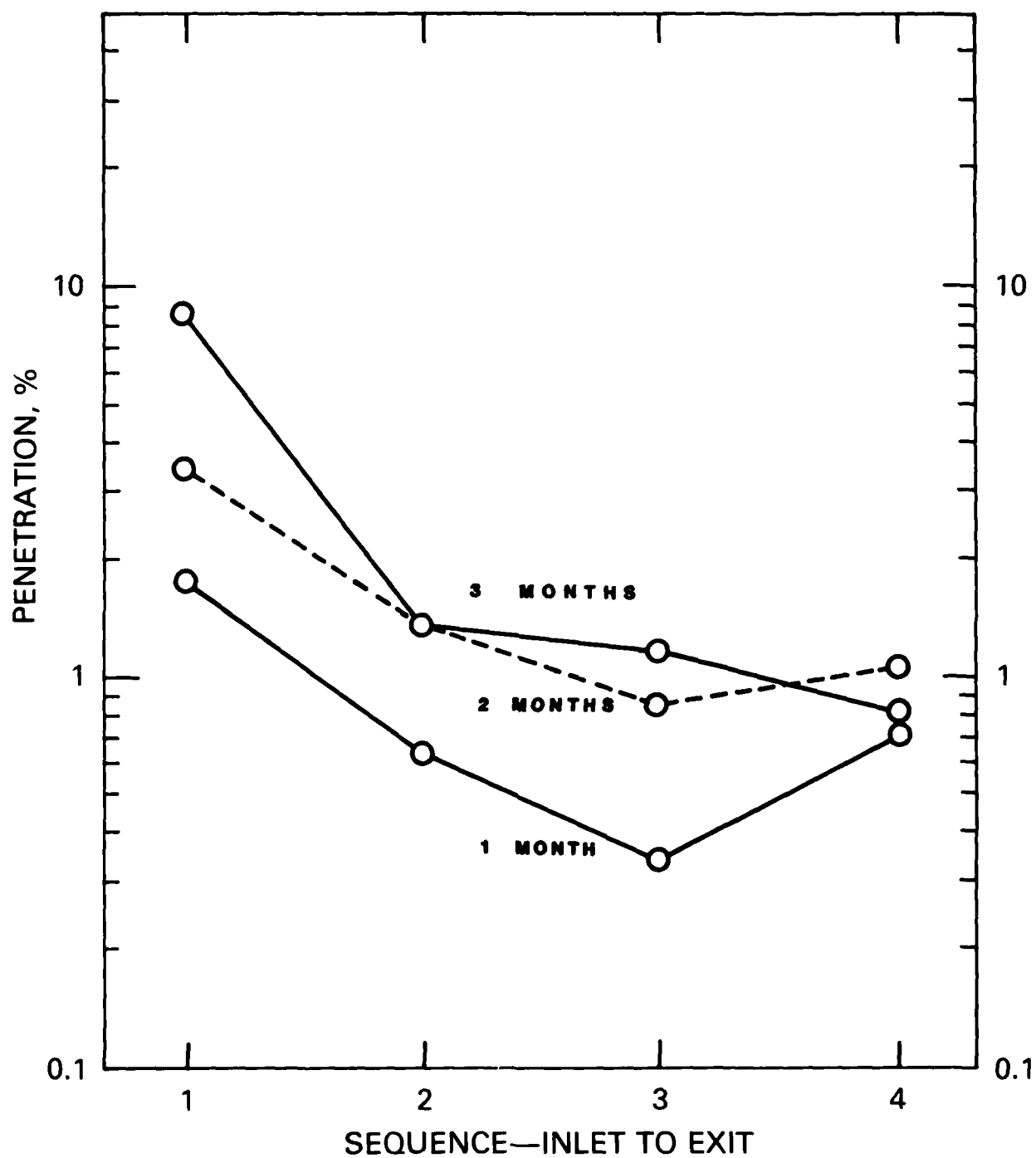


Figure 33. Profile in Weathering NACAR G 615 for One, Two and Three Months in Unmodified Outdoor Air at NRL

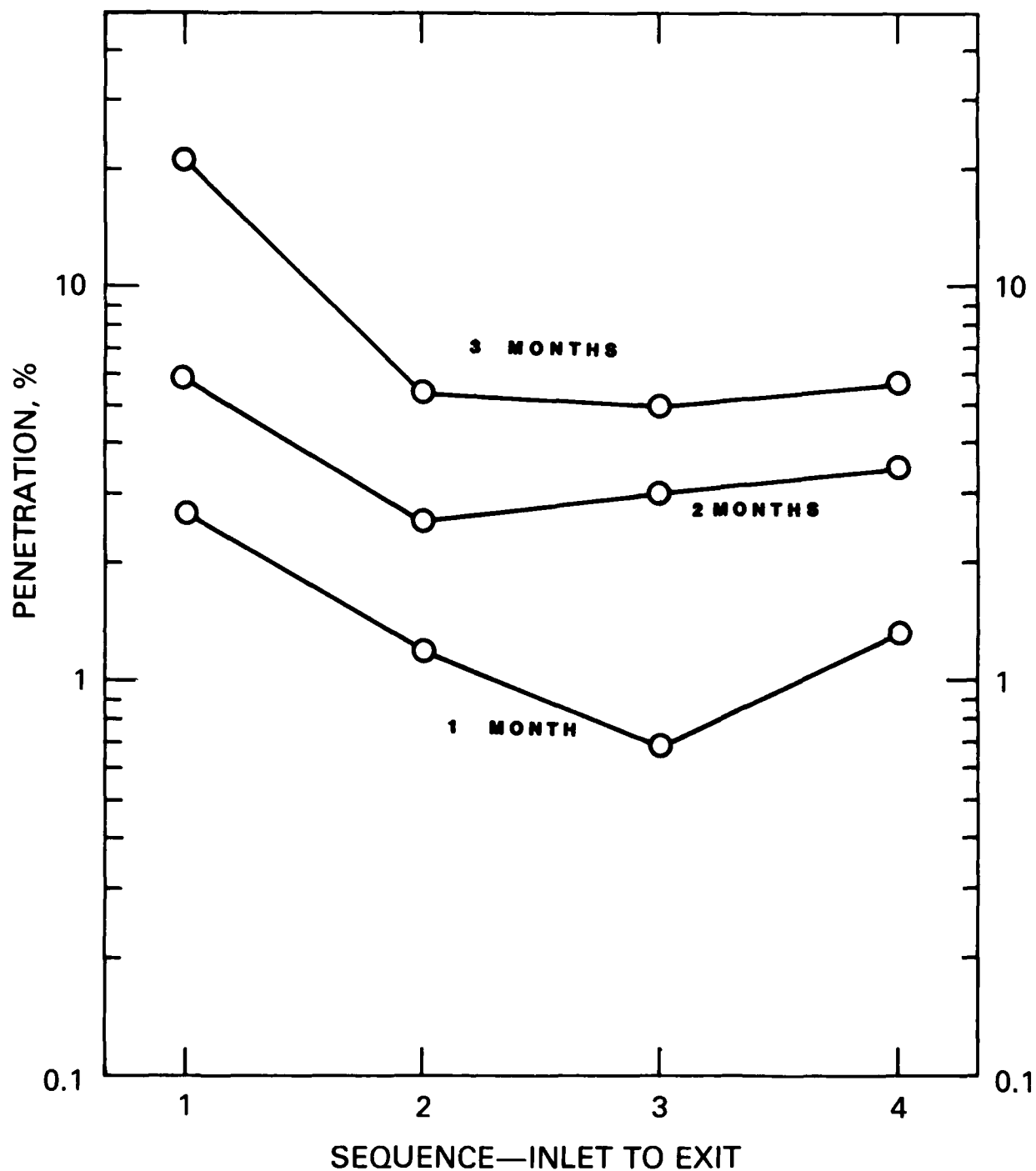


Figure 34. Profile in Weathering BC 727 for One, Two and Three Months in Unmodified Outdoor Air at NPL

For exposures of short duration, for example the laboratory tests of 100 hours at 100 L/min, the depth profile (see Fig. 35) indicates a fairly constant penetration value in layers 2, 3 and 4. The comparison is made for two carbons (BC 727 and G 615) using 70% RH air in one case and 70% RH and SO₂ in the second case. The standard deviation for the penetrations through the layers 2, 3 and 4 is within the overall experimental reproducibility of the measurements.

6.3 Chemical Changes in Nuclear Carbons Produced in Service

It has been demonstrated that a KI_x-impregnated carbon is modified in the weathering process and this causes a greater emission of iodine during a thermal analysis. The commercial nuclear carbon GX176 is impregnated with both KI_x and TEDA and a series of these carbons were kindly provided by the Savannah River Laboratory (17) after having been service-aged in the confinement system which received reactor building air (linear velocity of 15.8 m/min). The results demonstrate that the quantity of iodine emitted is greater in magnitude and occurs earlier in the heating cycle for the service-aged carbon than for the new carbon. Iodine could be detected at 50°C for the aged carbon as compared to 175°C for the new material.

A comparison is made (Fig. 36) between new GX-176 and the same carbon after 12-months service. The Y-coordinate is the integrated amount of iodine in micrograms that is emitted up to the designated temperature. During the thermal analysis test, the heating rate was 5.6°C/min and the air flow was 10 m/min.

The thermal instability of impregnated iodine induced by service ageing of GX-176 can be correlated with the measured penetration for both CH₃I-131 and I₂-131 (17). The results (Table 45) show that the two penetration values increase in about the same ratio (50 to 60). The thermal instability, as measured by the integrated iodine emission, is several magnitudes greater for the 12-month service-aged GX-176 than for the new material.

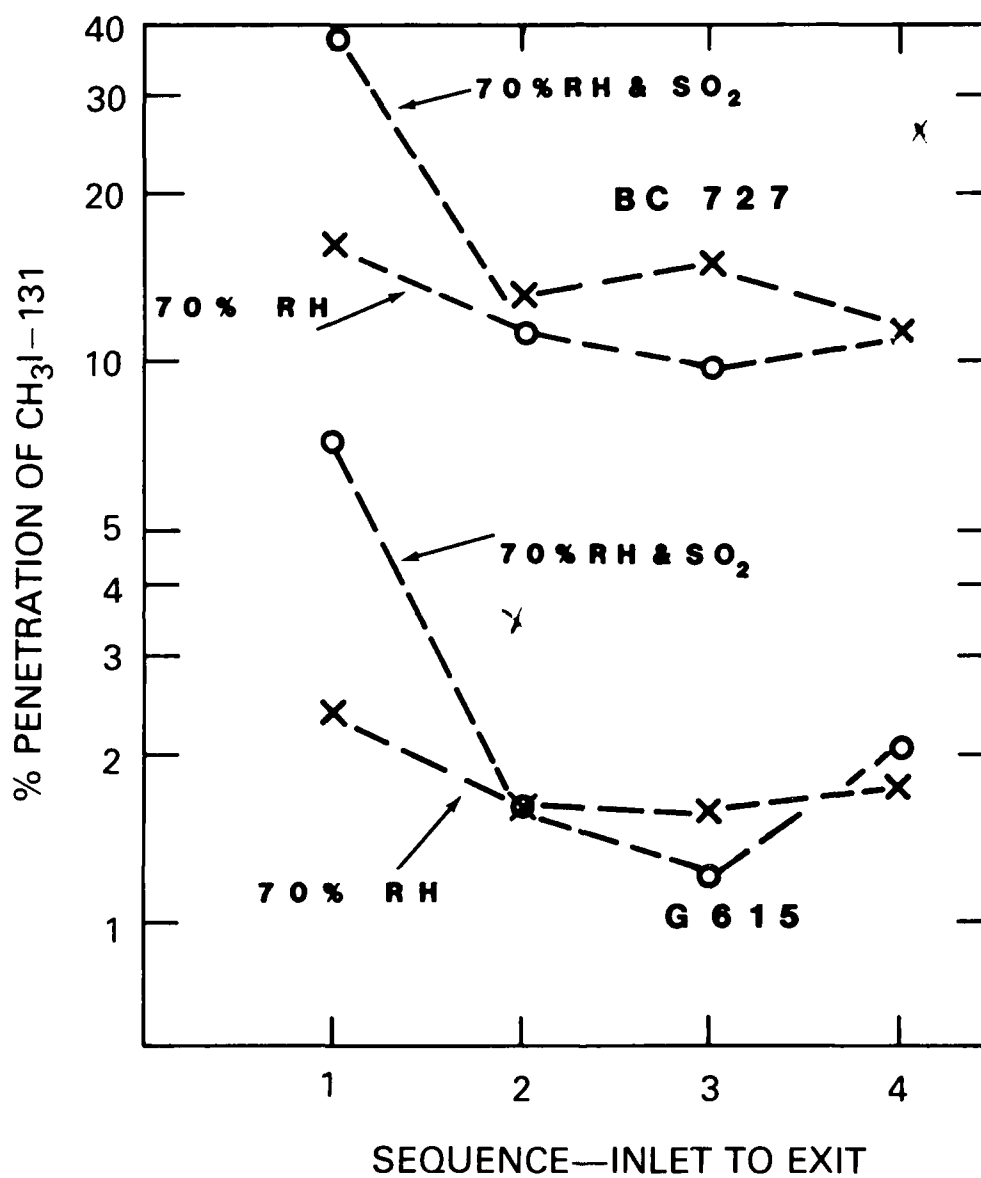


Figure 35. Profile Developed in Laboratory Flows of 100 L/min for 100 hrs with 70% RH + SO_2 and 70% RH alone

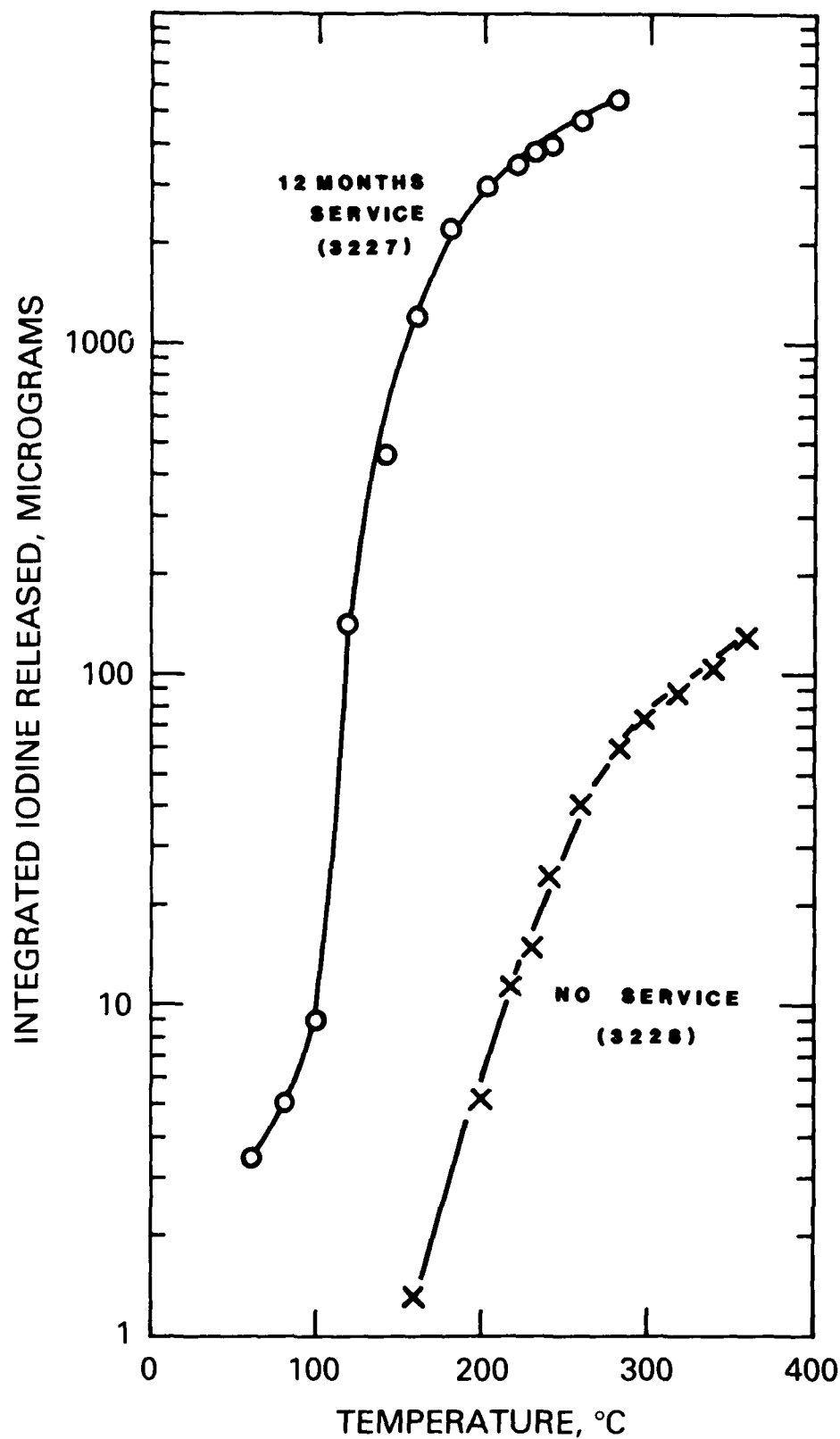


Figure 36. Emission of Iodine During Programmed Heating (5.6°/min) of GX-176 (KI and TEDA Impregnation)

Table 45. Properties of Service-Aged GX-176*

	New	12-month
Penetration CH_3I -131, %	0.45	28
Penetration I_2 -131, %	0.002	0.093
Iodine Emission:		
Integrated to 180°C, μg	1.3	2200
Integrated to 200°, μg	5.2	3000
Integrated to 250°, μg	31.0	4400

* A. G. Evans, Confinement of Airborne Radioactivity, DP-1463, Report January-December 1976.

6.4 Problems in Developing Test Procedures for Residual Life of Carbon Filters

Uniform procedures for the determination of iodine and methyl iodide penetrations for new impregnated activated carbons have been established for the nuclear industry by Subcommittee D-28.04 of the American Society of Testing Materials (ASTM). A summary tabulation (see Appendix 7) of these has been published (2). The specified parameters of the tests are the bed dimensions, flow rates, temperatures, relative humidities, pre-equilibration times, the $^{131}\text{ICH}_3$ feed period (temperature, relative humidity, concentration and duration of feed), and the elution period (temperature, relative humidity, flow rate, and duration).

The use of the ASTM testing procedures, designed to qualify new material, raises uncertainties when the tests are applied to weathered samples. The problem may be examined by noting the following general objectives and requirements of test procedures for activated carbons used in nuclear applications:

- (1) A means must be provided to make a decision when the activated carbon must be replaced.
- (2) The test must be demonstrated to be relevant to both plant operation and accident conditions.
- (3) The test must provide a capability to attain reproducible results.

- (4) The test results must not be negated by the action of specific contaminants that accumulate during service.

In adapting the ASTM procedures to weathered samples, it has been suggested that weathered nuclear carbons not be subjected to the 16-hour prehumidification with 95% RH air which is prescribed for new material. It is thought that the elimination of the prehumidification is more relevant to accident conditions since a carbon filter must be ready at all times to service its role as an engineered safety feature. Several investigators do not recommend any pretreatment that would bring about a partial regeneration of the carbon and increase the measured trapping efficiency. Should the regeneration be appreciable, the test results would be invalidated. Another suggested pretreatment is to store the sample as received in a static enclosure at 30°C over water for 24 hours, followed by a rapid transfer to the test container. In the present study, the testing of weathered samples has not been made with the 16-hour prehumidification.

The test carbons weathered at NRL with outdoor air are exposed on a time basis and accordingly are removed under the meteorological conditions existing at that time. The final days of an exposure may, therefore, occur during a very wet or a very dry period (see Appendix 8). A record of the dew points at NRL and in Chicago over the past nine years, shown in Appendix 9 and Appendix 10, combined with the changing daily temperature, establishes a variability in relative humidity that is beyond prediction. The test carbons from exposures completed during a period of dry weather have a small weight increase due chiefly to lack of ambient water vapor. When these samples were exposed to the 95% RH air during the $^{131}\text{I}\text{CH}_3$ testing, a significant temperature rise occurred. The rise was recorded by inserting a thermocouple in the air flow between the sample and backup beds. The temperature rise can be ascribed to the release of the heat of adsorption of water vapor on the test carbon. Some typical examples are given in Fig. 37 for a 30°C test and

in Fig. 38 for a 130° test. Because of the temperature gradients within the test carbon sample, there is a corresponding change in the linear air flow velocity and in the calculated contact time within the bed. Both changes are estimated to be approximately 1 to 3% for a temperature change of 10°C. The above observations are instructive for an understanding of the source of the temperature excursions within a test bed. When the test carbon sample was exposed to 90% RH air before testing, no temperature increase was observed as shown by the tabulated data for NRL Test 5088, given in Appendix 11. Relative to other sources of uncertainties, for example, the moisture content of the test carbons, the influence of the temperature gradient in the bed may not be significant. The temperature control specified by the ASTM test procedures need not be as precise for weathered samples as that specified to qualify a new carbon because of the above temperature excursions. It has also been noted that the designated control conditions specified by the ASTM Test Procedures (Appendix 7) apply only to the inlet air flow which is not representative of the sample temperature if moisture is being adsorbed.

When the weathering of a test carbon was completed during period of low relative humidity (<30% RH), it was possible to ameliorate the rise in temperature observed during $^{131}\text{ICH}_3$ testing in 95% RH air by first placing the test sample in a stainless steel wire basket and keeping it overnight over water in a static storage container. The procedure was successful in substantially minimizing the temperature rise in testing at 30°C; however, it is not known to what extent the procedure had influenced the observed value for penetration. Moreover, its significance to plant-scale carbon bed operation is not known. The consensus mentioned in a previous paragraph, namely to seek a testing procedure which predicts the response of a carbon during accident conditions, would require that a prehumidification technique not be used. Accordingly, after a number of tests that have been described, the above prehumidification technique in the wire basket was no longer used.

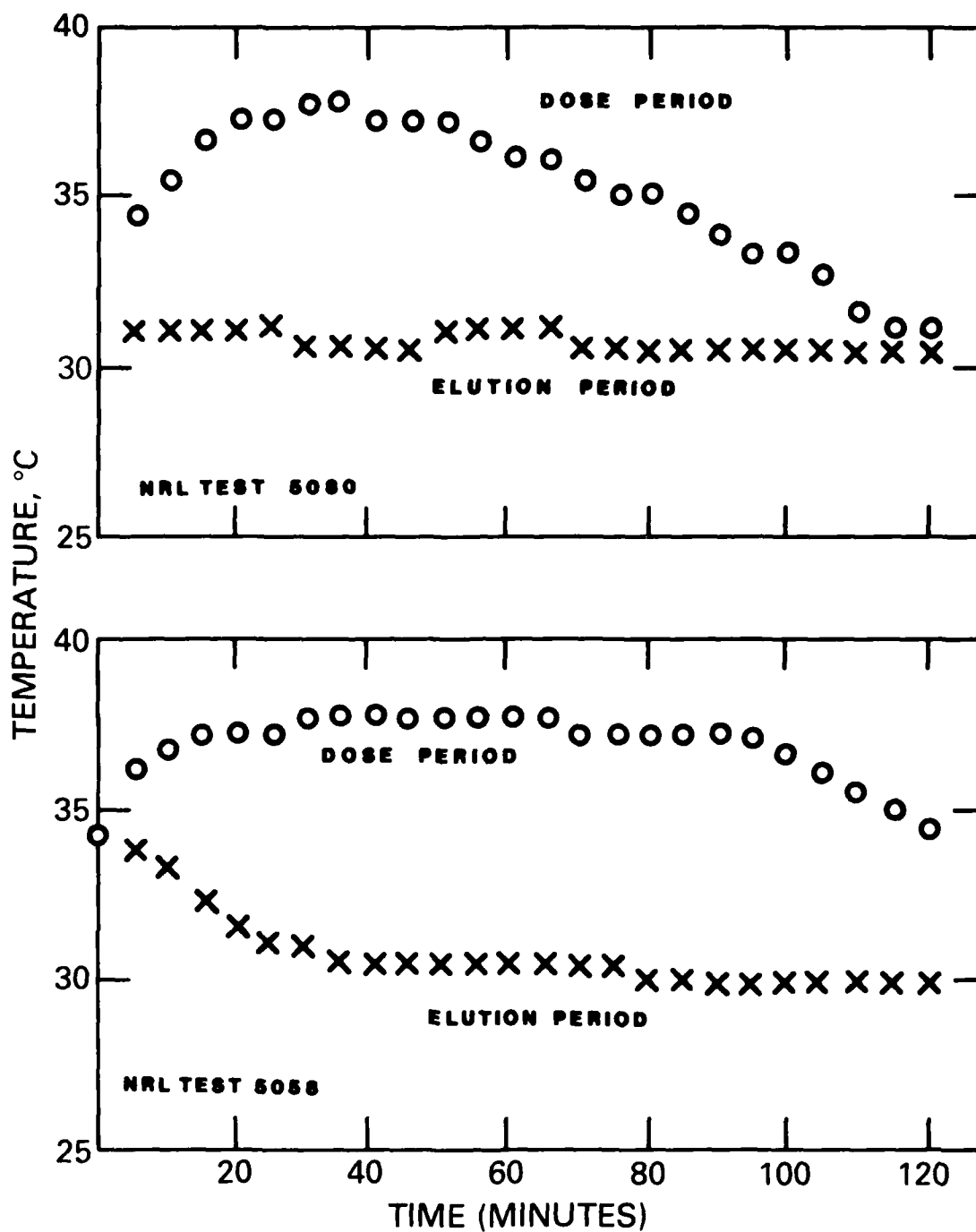


Figure 37. Temperature Excursion in Testing Weathered Nuclear Carbons at 30°C with Air at 95% RH

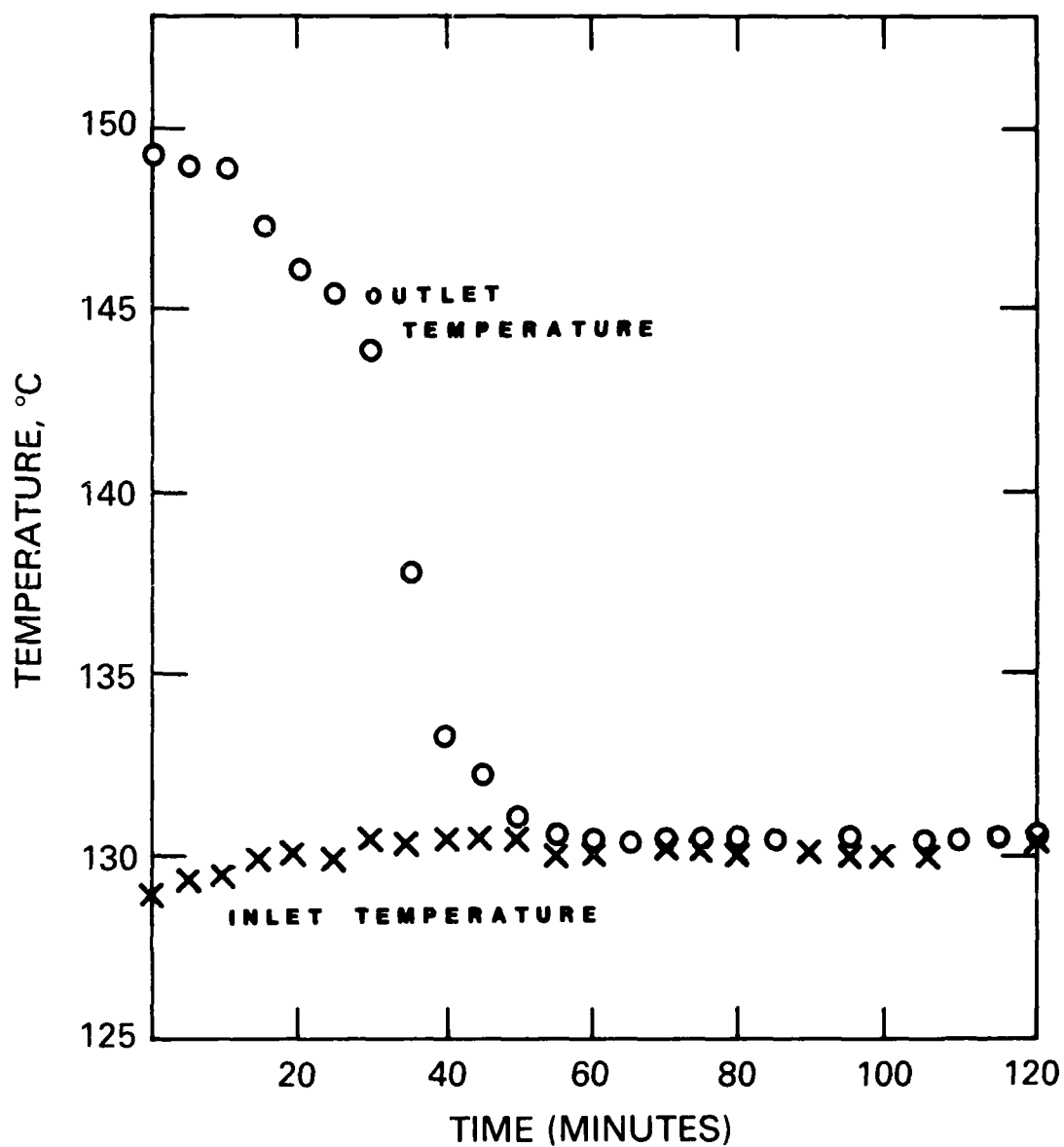


Figure 38. Temperature Excursions in Testing Weathered Nuclear Carbon at 130°C; the elution temperatures remained 130-130.5°C (thermocouple located between sample and backup beds)

Milham and Jones (25) observed a partial regeneration of BC 416, a non-impregnated coconut carbon, when the test bed was heated to 60°C for about 48 hours with purified air at 75 ft/min. After these conditions, some improvement was noted in the elementary iodine trapping efficiency. It may be noted that an air flow of 95% RH at 30°C drops to 22% RH at 60°C, which presents a different set of test parameters relative to that employed in the standard 30°C test procedure. Temperatures well above 60°C are necessary to reach a level of regeneration equivalent to new nuclear-grade carbon.

The accumulated experiences with weathered service carbons at NRL indicate that any prehumidification at 25 or 30°C before testing at 90% RH and 85% RH contributes to a further lowering in trapping efficiency relative to that observed without prehumidification. Thus, the use of a high relative humidity in the prehumidification of weathered service carbon can confuse the results of the subsequent measurement $^{131}\text{I}\text{CH}_3$ trapping efficiency. Table 46 summarizes some penetration results for a number of test carbons weathered at NRL and also a few carbons received after plant service. These were determined with and without prehumidification (16 hours in 95% RH air at 25 L/min). In all cases, the penetration is greater after prehumidification. When compared with the ASTM suggested performance requirements of new activated carbon (Appendix 7), six of the ten samples would not qualify when tested after preconditioning. There are several possible changes that could occur in test carbons during the prolonged exposure at high humidity air flows. Chemically, there are hydrolytic reactions and hydration changes among the impregnation constituents. Physically, the base carbon adsorbs water vapor in a strongly increasing amount with increase of relative humidity above about 40-50% (3). The behavior for a coconut nuclear carbon is shown in Fig. 39. A carbon filter, exposed accidentally to the vapors from solvent spills or to organic vapors from plant operations, is subject to synergistic interactions with water vapor.

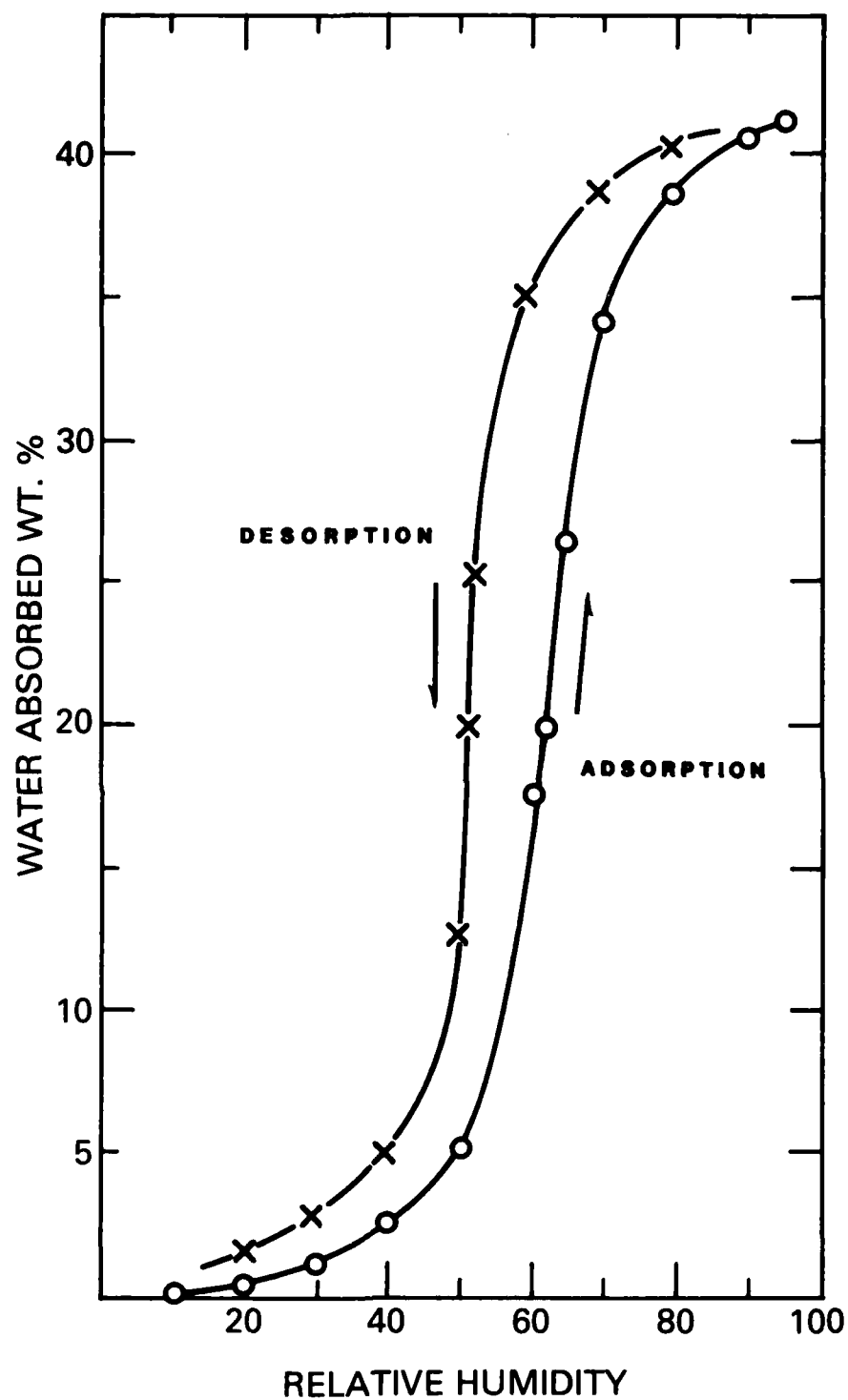


Figure 39. Dynamic Adsorption and Desorption of Water by Coconut Activated Carbon (NACAR G 210) at 25°C. (Kindly furnished by Frank Schwartz, Jr.)

Table 46. $^{131}\text{ICH}_3$ Penetration of Weathered Carbons and Those Removed from Service - Tested with and Without Prehumidification at 95% RH and 30°C

Carbon	Exposure	$^{131}\text{ICH}_3$ Penetration & Prehumidification	
		Yes	No
NRL 4289 on G202	4-29 Oct 76	6.74	0.73
NRL 4258 on MBV	1-30 Nov 76	1.10	0.22
SS (KI on 207B)	2-29 Dec 76	18.7	14.6
G-618	10-31 Jan 77	0.62	0.05
NRL 4230 on MBV	1 Feb-1 Mar 77	1.75	0.30
GX 176	2-31 Mar 77	0.89	0.45
BC 717	1 Apr-2 May 77	3.79	0.67
GX 176	Paint Fumes, 1 week	13.6	9.4
Used (not identified)	Removed from Plant	5.45	2.36
G 615	Removed from Plant	34.0	17.0

The above considerations may be summarized as follows:

- (1) The penetration of methyl iodide- 131 through nuclear-grade carbons depends on the moisture content of the carbon both in testing and in service operation.
- (2) When exposed to unmodified outdoor air, the moisture content of the carbon at the termination of the exposure contributes strongly to the test for the observed penetration.
- (3) The separate contributions of adsorbed contaminants and water vapor and the synergistic influence between the two components during weathering are critical factors that determine the efficiency at any given time during service.
- (4) The dew point, relative humidity, or moisture (g/M^3) are alternative parameters that correlate with the observed penetration of methyl iodide- 131 .

- (5) Intermittent air flow through test carbons may or may not result in the degradation of the trapping efficiency. The particular impregnation of the carbon appears to control the behavior.
- (6) Some engineering consideration should be given to the use of inlet air heaters to maintain the air in contact with the carbon at 70% RH or below.
- (7) The top $\frac{1}{2}$ inch layer of a 2-inch bed serves as a guard layer for the remaining carbon. The depth profile for new carbons show a simple exponential attenuation in the methyl iodide-131 penetration, but in weathered or service-aged carbons the depth profile is quite unpredictable.
- (8) The weathering of KI_x carbon in outdoor air modifies the thermal stability and during heating causes a greater emission of elemental iodine at lower initial temperatures. Similar behavior was observed with service-aged GX-176 which can be correlated with the measured penetration for both CH_3I -131 and elemental iodine-131.
- (9) The use of the ASTM iodine testing procedures designed to qualify new material, raises uncertainties when the tests are applied to weathered and service carbons.

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VIII. Appendix 1

Relationship between the ambient air temperature, relative humidity, and dew point.

Let t = the ambient temperature, $^{\circ}\text{F}$

p = the partial pressure water vapor at $t^{\circ}\text{F}$

p_o = the vapor pressure of water at $t_o^{\circ}\text{F}$

$$r = \text{relative humidity} = \left(\frac{p}{p_o}\right)_{t^{\circ}\text{F}} \quad (1)$$

$$\text{dew point (d.p.)} = \text{temperature } t_o \text{ at which } p = p_o \quad (2)$$

$$t^{\circ}\text{F} = (t^{\circ}\text{C} \times 1.8) + 32 \quad (3)$$

$$\log_{10} p_o = 8.10765 - \frac{1750.286}{235.0 + t_o^{\circ}\text{C}} \quad (4)$$

Using equations (1), (2), (3) and (4), any one of the three parameters r , d.p. ($^{\circ}\text{F}$) or $t(^{\circ}\text{F})$ can be expressed as a function of the other two. However, the calculation of d.p. from r and t and of r from d.p. and t are the most useful.

The dependence of dew point on relative humidity and temperature has been calculated and a graph useful in the range relevant to this report is given in Figure 40 (page 120). The moisture content of air as a function of temperature and relative humidity has been calculated and a graph useful in the range relevant to the report is given in Figure 41 (page 121).

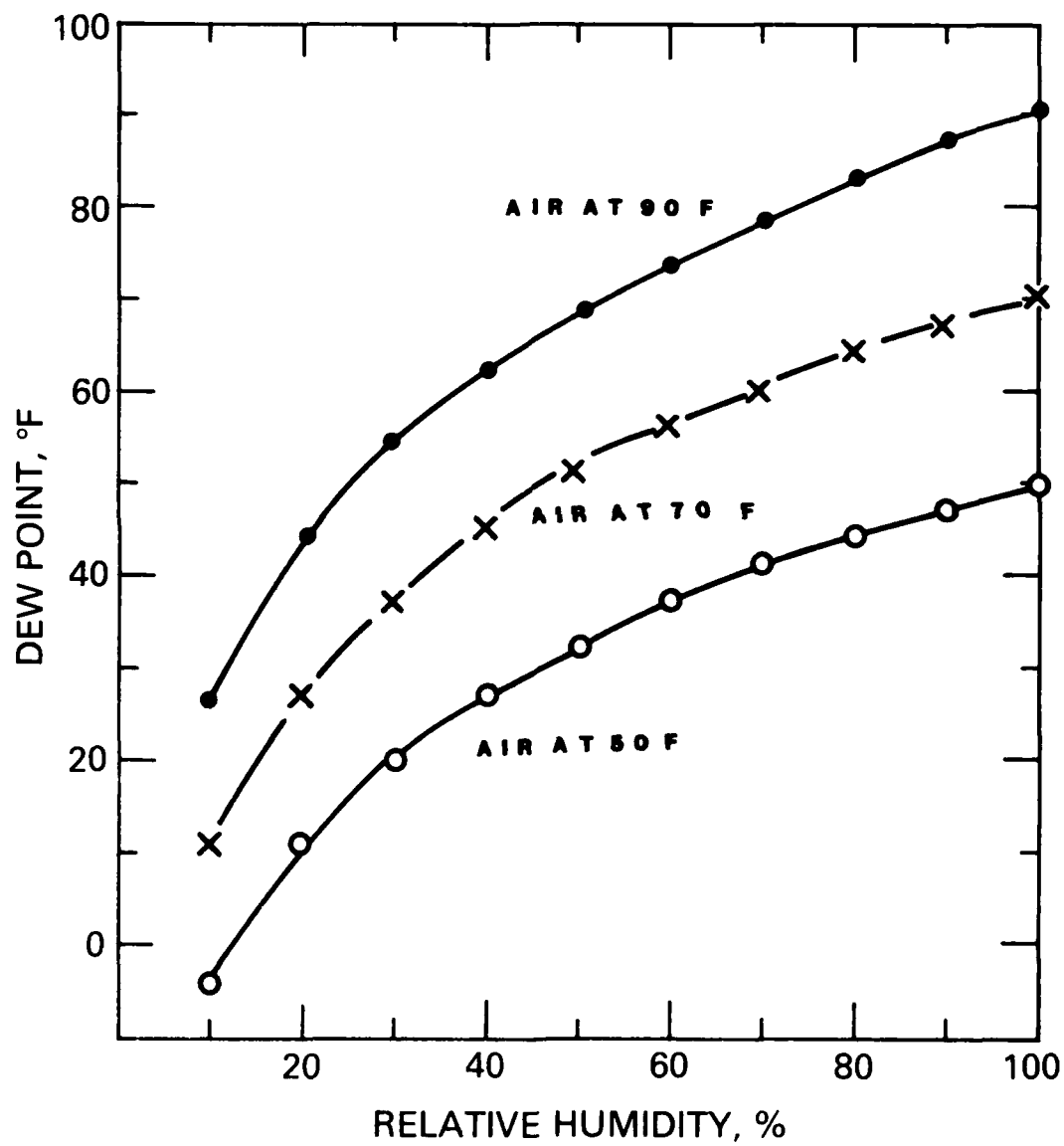


Figure 40. Dew Point Dependence on Relative Humidity and Temperature

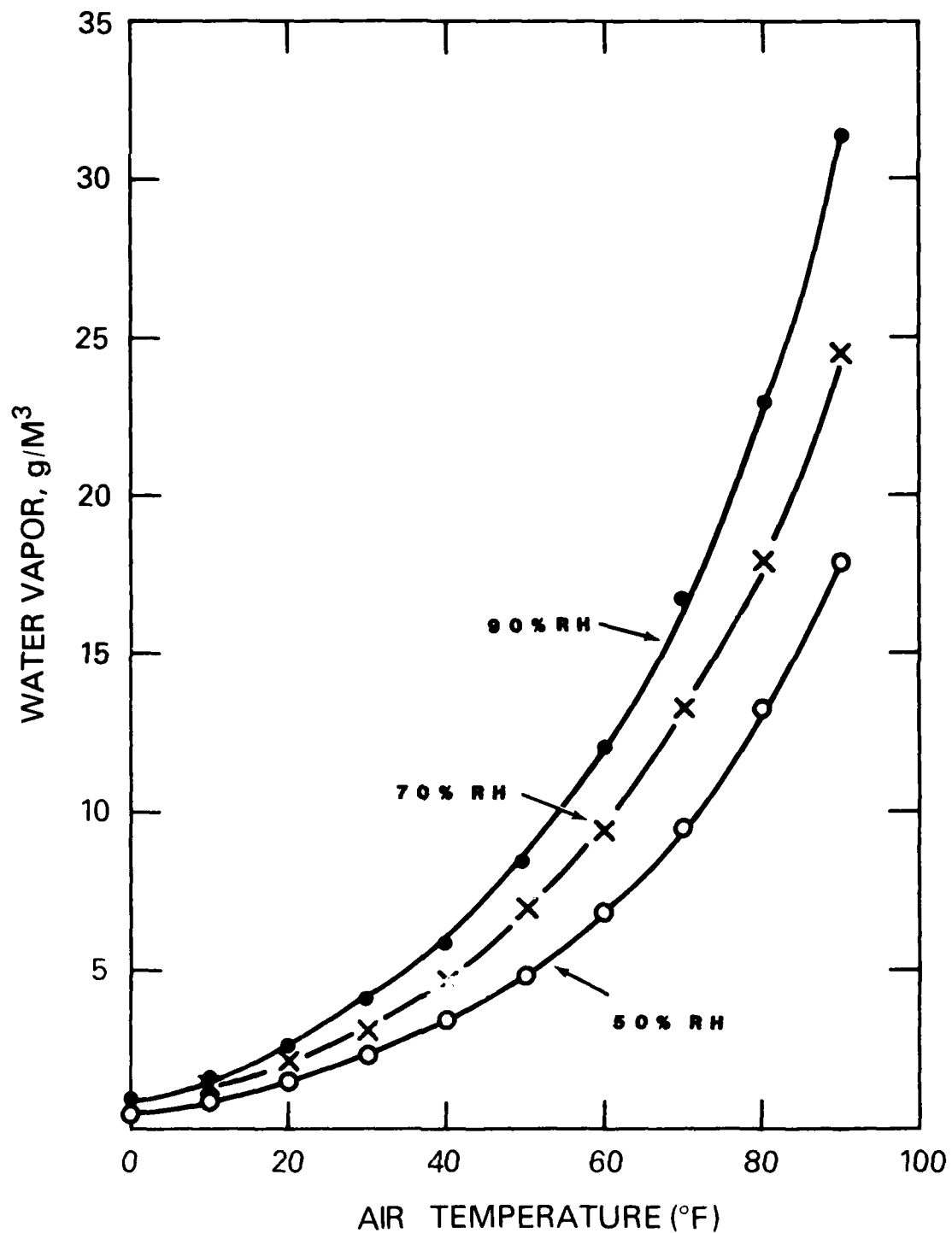


Figure 41. Moisture Content of Air as a Function of Temperature (0°-90°F) for Three Relative Humidities (50, 70, 90%)

Appendix 2

Table 47. Physical Properties of Some Impregnated Carbons
Used in Nuclear Power Plants (see Table 4)

Charcoal	#8	10	12	14	16	20	PAN	Nom. Size	Hard. (ASTM) %	Particle Diameter Change ²	Bulk ³ d.
BC 727	0.4	10.0	36.0	36.2	16.1	1.3	0.2	8x16	91.8	88.1	0.46
BC 717	0.9	6.6	27.2	41.2	21.8	2.2	0.1	8x16	97.3	94.1	0.51
G 615	1.4	10.5	30.8	40.5	15.4	1.0	0.3	8x16	97.4	96.4	0.54
G 617	0.5	6.9	35.4	43.5	11.6	1.8	0.2	8x16	96.8	93.5	0.43
MSA	0.9	7.5	30.8	42.2	17.4	1.0	0.2	8x16	98.6	97.4	0.56
AAF 2701	1.4	12.0	33.4	36.2	14.0	2.8	0.3	8x16	90.6	80.0	0.44
KITEG	0.2	9.9	40.3	34.4	13.4	1.2	0.6	8x16	95.7	94.6	0.42
SS (5% TEDA)	0	2.3	36.2	51.9	6.4	1.4	1.8	10x16	85.4	82.0	0.51

¹ASTM Hardness

²(Av. Particle Dia. after Hardness Test/Av. Before Test) x 100

³Density A.S.T.M. Procedure

Appendix 3 Penetration of $^{131}\text{ICH}_3$ at 21°C with NEW
Coconut Shell Commercial Nuclear Carbons
(Impregnated) With or Without Prehumidification

The penetration of methyl iodide was determined using the RDTM-16 procedure either with 16 hours of prehumidification at 95% RH or without this step. In both tests a 2-hour dose of methyl iodide and a 2-hour purge were made with 95% RH air. There is considerably less penetration without prehumidification, i.e., all adsorbent carbons behaved better without prehumidification. This raises a problem as to the evaluation of new carbons and carbons from service by the same procedure. The problem of water vapor in the testing procedure is discussed in 6.1.

Table 48. Penetration of $^{131}\text{ICH}_3$ at 21°C for New Commercial Carbons (Impregnated) With and Without Prehumidification

	Nominal Size	Water Extract pH	Penetration, % Prehumidification	
			16 Hours	None
BC 717	8x16	9.5	0.99	0.05
BC 727	8x16	9.5	4.8, 4.0	0.014
MSA 463563	8x16	8.5	2.5	0.13
NACAR G-615	8x16	9.8	0.27, 0.23	0.05
NACAR G-617	8x16	9.3	3.8	0.1
NACAR G-617-A	8x16	9.3	5.7	0.07

Note: Measurements made at NRL by C.H. Blachly

Appendix 4

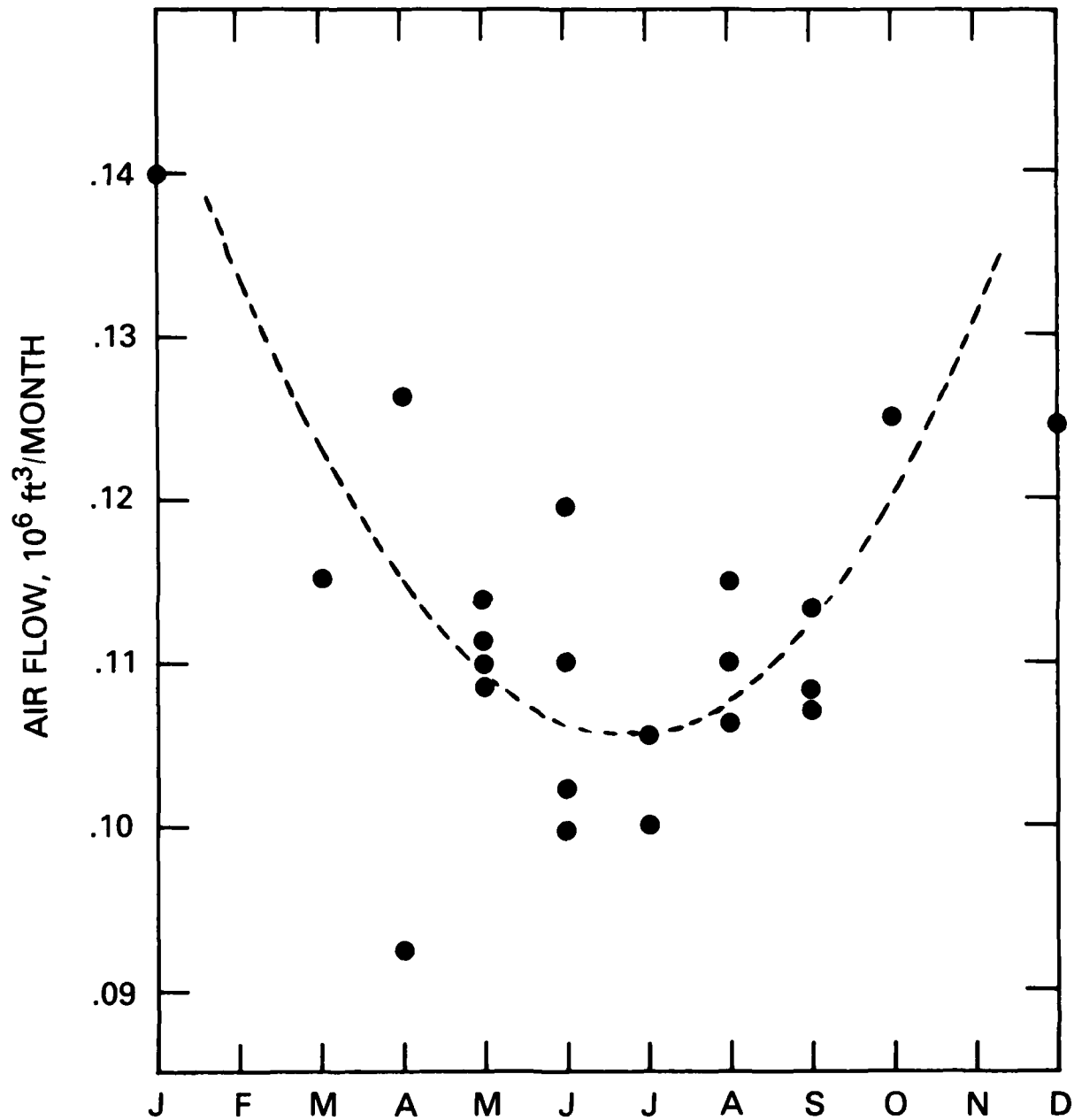


Figure 42. Monthly Variation of the Observed Air Flow through BC 727 in Same Exposure Configuration

Appendix 5

Table 49. Profile of Weight Increase at 21°C and the pH of the Water Extract after 100 hour Exposure in Air Flow of 100 L/min

Charcoal	% RH	% Wt. Increase in Layer				pH in Layer			
		1	2	3	4	1	2	3	4
BC 727	50	27.7	26.3	25.1	24.2	9.4	9.5	9.5	9.6
	70	45.4	45.3	45.5	45.3	7.7	9.2	9.1	8.8
	90	47.7	47.7	47.5	47.3	8.2	9.1	9.1	9.2
G 615	50	22.3	19.6	19.5	18.6	9.9	9.9	9.9	9.9
	70	28.6	28.5	28.6	28.6	9.0	9.5	9.6	9.6
	90	29.8	30.0	29.7	29.9	9.5	9.5	9.4	8.8
MSA 463563	50	23.2	21.5	20.7	20.1	8.2	8.3	8.3	8.3
	70	35.9	36.1	36.5	36.1	8.1	8.1	8.1	8.1
	90	38.4	38.9	39.9	38.7	8.3	8.3	8.3	8.2
S&S (5% TEDA)	50	16.2	15.4	15.3	14.8	8.4	8.4	8.4	8.4
	70	26.4	26.8	27.2	26.5	8.3	8.3	8.4	8.4
	90	31.7	31.7	31.9	32.1	8.6	8.7	8.7	8.7
AAF 2701	50	21.3	19.2	18.1	17.0	9.0	9.0	9.1	9.1
	70	44.1	44.2	43.3	43.0	8.7	8.5	8.6	8.6
	90	51.0	51.3	51.5	52.2	8.7	8.7	8.7	8.7
G 617	50	22.7	20.5	19.6	18.6	9.4	9.4	9.4	9.5
	70	58.2	58.3	55.9	57.0	9.2	9.2	9.2	9.2
	90	61.9	60.6	63.0	60.3	9.6	9.6	9.6	9.6
KITEG	50	19.5	18.8	18.3	17.8	7.6	7.6	7.7	7.7
	70	28.6	28.3	29.7	29.8	7.7	7.6	7.7	7.7
	90	38.8	39.6	40.5	41.3	7.8	7.7	7.7	7.7

Appendix 6

Certified Permeation Tubes, Length 10 cm,
Used as Chromatograph Standards (Analytical
Instrument Development, Inc., Westchester,
PA 19380)

Tube	Compound	Temperature °C	Certified nanog/min.
4131	methyl iodide	30	270
4222	methyl iodide	30	300
5651	methyl iodide	30	1460
5653	hexane	70	5770
5655	carbon tetrachloride	70	6550
5657	benzene	70	6710
5659	methanol	70	4470
7362	methyl ethyl ketone	70	1510
7363	methyl ethyl ketone	30	295
7365	toluene	70	1040

Appendix 7: Summary Radioiodine/Methyl Iodide Standard Test
Methods of ANSI/ASTM D3803-79

Section	3.1 Methyl Iodide Penetration 30°C 95% RH	3.2 Methyl Iodide Penetration 80°C 95% RH	3.3 Methyl Iodide Penetration 130°C 95% RH	3.4 Elemental Iodine Penetration 30°C 95% RH	3.5 Elemental Iodine Retention	Units
Test Adsorbate	(CH ₃ 127 I + CH ₃ 131 I)	(127 I + CH ₃ 131 I)	()	(127 I ₂ + 131 I ₂)	()	
Test Adsorbate Concentration	1.75±0.25	1.75±0.25	1.75±0.25	17.5±0.5	75±5	mg/m ³
Equilibration Period:	Temp	30.0±0.5	80.0±1.0	30.0±1.0	30±5	°C
	RH	95±2	(Note a)	95±2	(Note a)	%
	Duration	16.0±0.5	0	16.0±0.5	0	hr
Feed Period	Temp	30.0±0.5	80.0±0.5	30.0±0.5	30±5	°C
	RH	95±2	95±1	95±1	Ambient	%
	Duration	120±1	60±1	120±1	10.0±0.2	min
Elution Period:	Temp	30.0±0.5	80±0.5	30.0±0.5	180±3	°C
	RH	95±1	95±1	95±1	NA	%
	Duration	240±1	240±1	240±1	240±1	min
Absolute Pressure	(Note c)	104±5	104±5	104±5	104±5	kPa
Gas Velocity	12.2±0.5	12.2±0.5	12.2±0.5	12.2±0.5	12.2±5	m/min
Bed Depth	(Note d)	50±1	50±1	50±1	25±1	mm

Above list is standard for adsorption media used in 50 mm bed depth tray filters, as described in AACC CS-8 and for media used in other bed depths and operated at the same gas velocity (12.2±0.5 m/min). For other operating velocities and for all media to operate at conditions substantially different from the above, any deviations from the above list must be specified.

Appendix 7 (Cont'd)

NOTES:

- a. For each of these tests, the test bed is brought to the listed equilibration temperature without air flow before other phases of the test begin. For tests 3.2 and 3.5 this thermal equilibration is the only equilibration. For tests 3.1, 3.3 and 3.4, humid air at the stated temperature and humidity is passed through the beds for the stated period following bed warm-up.
- b. For test 3.3, humid air flow is maintained for 2.0 ± 0.1 hr, or until the upstream/downstream dry-bulb temperature differential is less than 2°C .
- c. $101 \text{ kPa} = 1 \text{ atm}$. Tests 3.1, 3.2, 3.4 and 3.5 are run slightly above one atmosphere to allow for a blow-through system with flow measurement, demister, etc.
- d. The test bed for tests 3.1 - 3.4 may be a single canister of full depth, or two 25 mm deep canisters in series. For test 3.5, a single 25 mm deep canister is used.

Appendix 8

Observations of Relative Humidity % and Dew Points ($^{\circ}\text{F}$) at
3-hour Intervals During the 48 Hours
Before Charcoal Sampling

Date	Hour	% RH	d.p.- $^{\circ}\text{F}$	Date	Hour	% RH	d.p.- $^{\circ}\text{F}$
2 May	13	28	29	4 Feb	13	36	6
	10	37	28		10	44	5
	7	48	27		7	57	6
	4	51	26		4	55	8
	1	44	25		1	47	9
1 May	22	32	23	3 Feb	22	47	10
	19	23	19		19	47	11
	16	20	19		16	39	10
	13	23	21		13	41	10
	10	24	18		10	47	11
	7	30	18		7	62	11
	4	32	19		4	63	13
	1	23	17		1	69	16
30 April	22	23	20	2 Feb	22	63	17
	19	26	29		19	63	18
	16	31	40		16	67	22
1 June	13	40	61	10 Aug	13	59	70
	10	51	61		10	69	71
	7	62	60		7	93	71
	4	71	60		4	93	71
	1	84	65		1	90	70
31 May	22	76	65	9 Aug	22	87	70
	19	67	65		19	83	71
	16	65	70		16	55	69
	13	79	70		13	52	69
	10	76	67		10	61	70
	7	79	66		7	85	74
	4	87	65		4	91	74
	1	79	65		1	85	74
30 May	22	69	63	8 Aug	22	72	73
	19	65	67		19	68	74
	16	50	65		16	63	73

Appendix 9

Dew Points, °F (Monthly Average) Recorded
at the Washington National Airport

	1971	1972	1973	1974	1975	1976	1977	1978	1979
January	19	27	23	31	29	20	12	18	22
February	25	23	23	23	28	29	23	15	15
March	25	30	40	31	29	35	36	28	36
April	33	39	42	41	34	38	44	35	42
May	49	53	50	51	56	49	56	52	57
June	64	59	65	60	62	60	59	61	62
July	64	67	66	64	66	64	67	67	69
August	64	65	67	67	67	66	68	71	70
September	63	61	60	59	59	60	63	60	65
October	57	44	48	42	52	46	44	45	50
November	36	35	36	36	41	29	40	40	44
December	34	33	29	31	28	22	26	28	30

Appendix 10

Observations of Dew Points, °F (Monthly Average)
at the Chicago O'Hare International Airport

	1971	1972	1973	1974	1975	1976	1977	1978	1979
January	9	11	21	18	21	13	1	9	6
February	20	14	22	19	20	25	17	10	10
March	25	23	35	29	25	31	32	24	31
April	32	35	38	39	33	37	38	35	35
May	41	48	44	47	50	43	50	47	46
June	60	53	59	55	61	56	53	56	55
July	58	62	64	61	61	60	63	63	59
August	59	65	65	61	64	57	60	62	61
September	58	57	57	49	50	49	57	58	52
October	51	41	50	41	43	36	43	41	41
November	30	32	34	33	39	20	33	33	30
December	28	20	23	25	25	11	18	20	23

Appendix 11

Temperatures Observed Between Sample and Back-up Beds
during Methyl Iodide-131 Penetration Test at 95% RH for
Sample #5088 (1,2,3,4), Weathered at 90% RH

	TIME	TEMPERATURE °C		%RH		TIME	TEMPERATURE °C		%RH
		INLET	OUTLET				INLET	OUTLET	
FEED CH ₃ I	1300	29.5	30.0	94.4	PURGE ON	1500	30.0	30.0	94.4
	1305	29.5	30.0	94.4		1505	30.0	30.0	94.4
	1310	29.5	29.5	94.4		1510	30.0	30.0	94.4
	1315	29.5	29.5	94.0		1515	30.0	30.0	94.4
	1320	29.5	29.5	94.0		1520	30.0	30.0	94.4
	1325	29.5	29.5	94.0		1525	30.0	30.0	94.4
	1330	30.0	30.0	94.4		1530	30.0	30.0	94.4
	1335	30.0	30.0	94.4		1535	30.0	30.0	94.4
	1340	30.0	30.0	94.4		1540	30.0	30.0	94.4
	1345	30.5	30.5	94.4		1545	30.0	30.0	94.9
	1350	30.5	30.5	94.9		1550	30.0	30.0	94.5
	1355	30.5	30.5	94.9		1555	30.0	30.0	94.4
	1400	30.5	30.5	94.9		1600	30.0	30.0	94.0
	1405	30.5	30.5	94.4		1605	30.0	29.5	94.4
	1410	30.5	30.5	94.4		1610	30.0	30.0	94.9
	1415	30.5	30.5	94.4		1615	30.0	30.0	94.4
	1420	30.5	30.5	94.4		1620	30.0	30.0	94.4
	1425	30.5	30.5	94.4		1625	30.0	30.0	94.4
	1430	30.0	30.5	94.9		1630	30.0	30.0	94.4
	1435	30.0	30.5	94.9		1635	30.0	29.5	94.4
	1440	30.0	30.5	94.4		1640	30.0	30.0	94.4
	1445	30.0	30.5	94.4		1645	30.0	30.0	94.9
	1450	30.0	30.0	94.4		1650	30.0	30.0	94.9
	1455	30.0	30.0	94.9		1655	30.0	30.0	94.9
FEED OFF	1500	30.0	30.0	94.9	PURGE OFF	1700	30.0	30.0	94.9

NRL SAMPLE = 0.140 (1) $\mu\text{Ci} \pm 0.23\%$

Backup A = 0.108 (0) $\mu\text{Ci} \pm 0.39\%$

Backup B = 0.723 (-3) $\mu\text{Ci} \pm 4.34\%$

NRL Penetration = (7.21 \pm 0.05)%

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16. ABSTRACT <i>(200 words or less)</i> <p>The useful life of activated carbon filters in engineered safety-feature and normal ventilation systems of nuclear power stations is slowly impaired by the contaminants accumulated from the large volume of air in process. In this study eight commercial impregnated carbons were exposed to unmodified outdoor air at NRL for different periods up to one year and to air flows of known contaminant species and concentrations under controlled laboratory conditions, both followed by measurements of the methyl-iodide-131 penetration. Two of the carbons were exposed to outdoor air at the Argonne National Laboratory and at the Simi Valley Monitoring Station. The test carbons included commercial impregnations of potassium iodide with or without elemental iodine and of tertiary amines, either separately or as co-impregnates. Air flows above 70 RH degrade the carbon efficiency significantly. Also, an adverse synergistic influence of moisture and hydrocarbon vapors has been observed. The entrance layer of test charcoals were found to be most significantly affected by the exposure insult. The gradient in methyl iodide-131 penetration through the bed changes from a simple exponential profile for new carbons to a non-linear exponential profile for weathered and service-aged carbons.</p>					
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